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16. ABSTRACT

The report gives results of chemical analyses of whole coal samples, bench samples (vertical), and washed coal samples. Most of the samples were from the Illinois Basin, but other U.S. coal producing areas are also represented. In addition to the standard analyses of coal parameters, approximately 60 elements were also analyzed. Statistical analysis of the whole coal samples data indicates that elemental concentrations tend to decrease from the Eastern to Western coals; elements with the greatest variation are identified with the discrete mineral matter; those with the least, with the organic matter. The bench samples indicated wide variations in elemental concentrations within a single coal seam: the greatest differences were found in the top and bottom of the seam. The trace elements were classified into four organic affinity groups, based on the analytical data: organic, intermediate-organic, intermediate-inorganic, and inorganic.

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Coal	**Trace Elements**	**08G,21D**
Chemical Analysis	**Elemental Concentrations**	**07D**
Chemical Elements		**07B**
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TRACE ELEMENTS IN COAL: OCCURRENCE AND DISTRIBUTION

by

H.J. Gluskoter, R.R. Ruch, W.G. Miller,
R.A. Cahill, G.B. Dreher, and J.K. Kuhn

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R. A. Cahill, G. B. Dreher, and J. K. Kuhn

ABSTRACT

Chemical analyses of 172 whole coal samples, 50 (5 sets) bench samples (vertical segments of the seam), and 54 (9 sets) washed coal samples (separated by specific gravity methods) have been made by the Illinois State Geological Survey. One hundred and fourteen of the 172 whole coal samples were from the Illinois Basin, as were all of the bench samples and 5 of the 9 sets of washed coals. The remaining samples were from other coal-producing areas of the United States.

Elements determined by chemical analyses were aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), boron (B), bromine (Br), cadmium (Cd), calcium (Ca), carbon (C), cerium (Ce), cesium (Cs), chlorine (Cl), chromium (Cr), cobalt (Co), copper (Cu), dysprosium (Dy), europium (Eu), fluorine (F), gallium (Ga), germanium (Ge), gold (Au), hafnium (Hf), hydrogen (H), indium (In), iodine (I), iron (Fe), lanthanum (La), lead (Pb), lutetium (Lu), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), nitrogen (N), oxygen (O), phosphorus (P), potassium (K), rubidium (Rb), samarium (Sm), scandium (Sc), selenium (Se), silicon (Si), silver (Ag), sodium (Na), strontium (Sr), sulfur (S), tantalum (Ta), terbium (Tb), thallium (Tl), thorium (Th), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V), ytterbium (Yb), zinc (Zn), and zirconium (Zr). In addition to the 60 elements, the samples were analyzed for the standard coal parameters. Analytical methods included neutron activation analyses, atomic absorption spectroscopy, X-ray fluorescence spectroscopy, optical emission spectroscopy, and ion selective electrode analyses.

Statistical analyses of this large quantity of data on whole coal samples have allowed for many generalizations to be drawn including:

1. Elemental concentrations tend to be highest in coals from the Appalachians, lowest in coals of the Western United States, and intermediate in coals from the Illinois Basin.

2. Elements that have the largest ranges in concentrations are those that are found in distinct mineral phases in the coals; elements with narrow ranges are often those found in organic combination in coal.

3. Only four elements are, on the average, present in coals in concentrations significantly greater than the clarke of those elements (average concentration in the earth's crust). These are boron, chlorine, selenium, and arsenic. Not all are concentrated in each of the samples analyzed from the three geographic groups (eastern U.S., western U.S., and the Illinois Basin).

4. Most of the elemental concentrations in coals are lower than the clarke of the elements.

5. Boron is concentrated only in the coals of the Illinois Basin; possibly the presence of boron represents a greater marine influence during and immediately following the time of the coal swamp in the basin.

Generalizations from the statistical analyses of the analytical data from five bench sets from the Illinois Basin include the following:

1. Wide variations in elemental concentrations are present between benches of a single coal sampled.

2. Although elements may be concentrated within any bench of a coal, concentrations are more commonly observed at the top and/or bottom of the coal seam.

3. Germanium is concentrated in the top and bottom benches of four of the five bench sets.

4. Most elements occur in significantly higher concentrations in the fine-grained sedimentary rocks associated with the coal (roof shales, underclays, and partings) than in the coal.

An index of organic affinity of the elements was calculated from cumulative curves (washability curves) of the data determined on specific gravity fractions of the washed coals. Elements have been classified as "organic", "intermediate-organic", "intermediate-inorganic", and "inorganic", on the basis of value of the organic affinity index. Coals of the Illinois Basin are quite similar in this regard. The following generalizations are suggested:

1. Germanium, beryllium, boron, and antimony are classified within the organic group in all samples. Germanium has the highest value of organic affinity in each coal.

2. Zinc, cadmium, manganese, arsenic, molybdenum, and iron are within the inorganic group in all four samples.

3. A number of metals including cobalt, nickel, copper, chromium, and selenium have organic affinities within the intermediate categories. This suggests a partial contribution from sulfide minerals in the coal but also suggests the presence of these elements in organometallic compounds, as chelated species, or as adsorbed cations.

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INTRODUCTION

Within recent years the general public and the scientific community have become increasingly aware of the problems of energy and environment that directly affect the activities of people in the United States. The problems are not separate and distinct, but rather are associated intimately with each other. To maintain a standard of living similar to that which has evolved in the United States will require the increased development of a domestic source of energy. To preserve the quality of life to which everyone aspires will necessitate production of that energy in an environmentally acceptable manner.

Coal is the most abundant fossil fuel resource in the United States (Simon and Malhotra, 1976). Energy from coal will continue to be extracted in the "normal" way by direct combustion in steam boilers and generation of electricity. However, extensive research is being done to find efficient methods of producing clean and easily handled gaseous and liquid fuels from coal. Coal is composed not only of those elements generally considered to be organic (C, H, O, and N), which are utilized in converting coal to synthetic fuels, but it is extremely heterogeneous and contains significant quantities of "inorganic" elements. These inorganic elements are associated primarily with individual mineral phases in the coal. The term "mineral matter" is often used to refer to all the inorganic constituents of coal.

Mineral matter, including major, minor, and trace elements, composes a significant proportion of coal. It is difficult to precisely measure the quantity of mineral matter in coal. For the purposes of this study the amount of radio-frequency low-temperature ash produced in a radio-frequency asher at temperatures below 150°C (Gluskoter, 1965b; Rao and Gluskoter, 1973) will be assumed to equal

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Note: Trace Elements in Coal: Occurrence and Distribution, Gluskoter et al., has also been published in 1977 as Circular 499 by the Illinois State Geological Survey, Urbana, IL 61801.

the mineral matter of the coal. In the coal samples reported in this study, the mineral matter ranges from 3.8 percent to 31.7 percent with a mean value of 15.3 percent. Before the significance of this proportion of the coal can be intelligently assessed, accurate determinations of the various elements contained in the ash must be made.

The Illinois State Geological Survey has had a continuing research effort on the chemistry of coal for nearly seventy years. Within the past six years, efforts have been concentrated on the analyses of coal for trace elements. These efforts have resulted in a number of publications, including: Ruch et al., 1971, 1973, 1974; Gluskoter and Lindahl, 1973; Gluskoter, 1975; Frost et al., 1975; Kuhn et al., 1975; and Dreher and Schleicher, 1975.

During the period 1972-1976, these efforts were partially supported by the U.S. Environmental Protection Agency. This report summarizes all the analytical data collected during the period of that support. In part, it duplicates material in previous publications (for example, Ruch et al., 1973, 1974).

The initial effort (Ruch et al., 1973,1974) involved a comprehensive characterization of 101 coals of the United States, most of which were from the Illinois Basin. The initial study included development and refinement of specific chemical and mineralogical methods of analysis, new methods for sample pretreatment, volatilization studies, and more efficient methods for treatment of the data. The study laid the foundation for many geochemical conclusions, but also indicated the necessity for further work.

The present project is concerned with the analyses of 71 additional U.S. coals, more than half of which are from the eastern and western coal-producing areas; the remainder are from the Illinois Basin (fig. 1). The study also includes 40 bench samples (vertical segments within a coal seam) representing five geologically different environments from the Illinois Basin, and 32 float-sink samples (gravity fraction separations) from five coals that are geographically widely separated and that differ significantly both geologically and chemically.

The scope of the work was extended in this study to include the determinations of 23 additional elements, many of which had not had their distributions in coal characterized previously. These analyses were made possible by advances in analytical methods, especially by the acquisition of a high-resolution detector for instrumental neutron activation analysis (INAA). The 71 whole coal samples, the 40 bench samples, and the 32 washed coal samples were analyzed for these 23 additional elements, as were twenty-five samples from the Herrin (No. 6) Coal Member of Illinois, selected from the group of 101 coals previously analyzed.

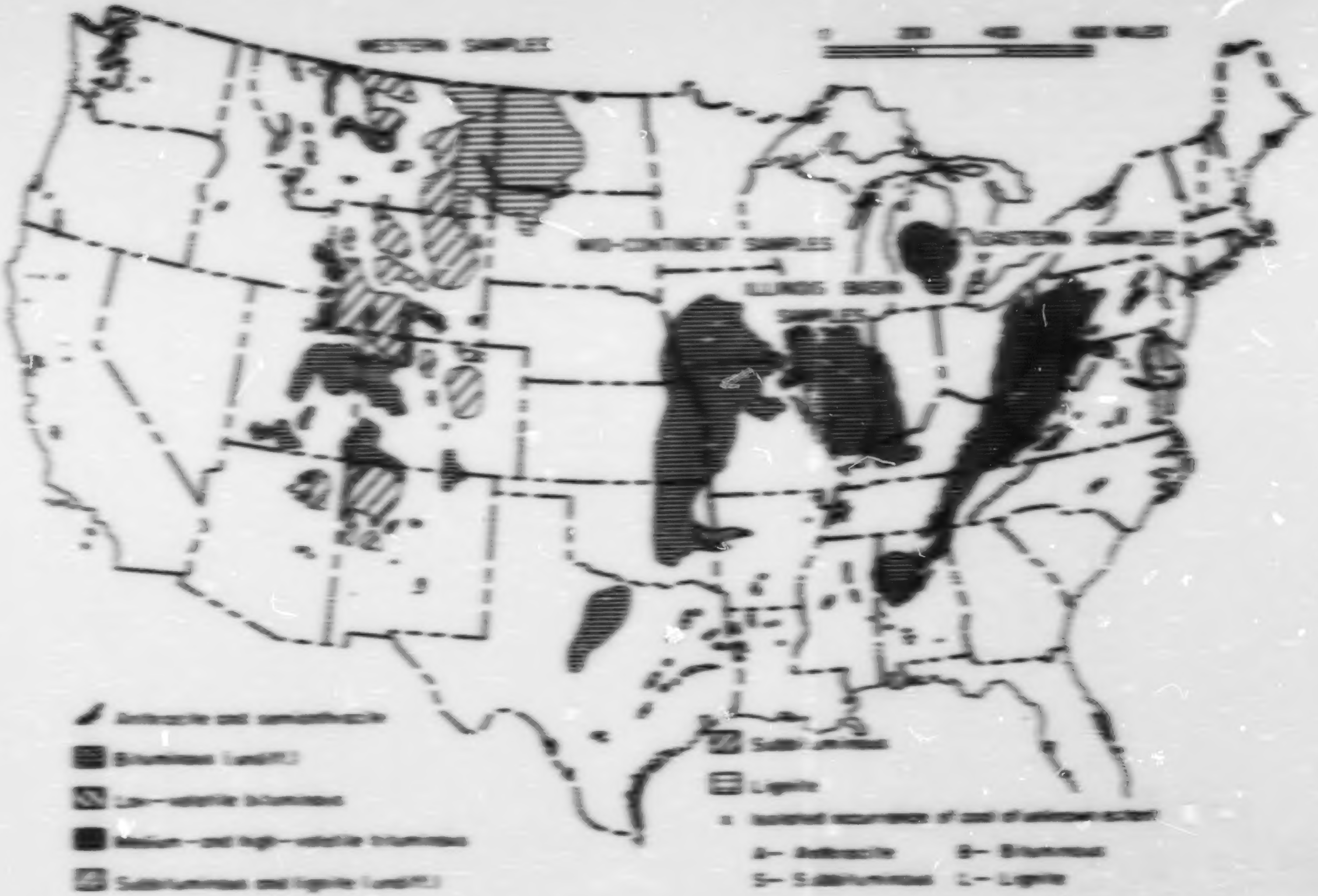
WESTERN SAMPLES
0 200 400 600 MILES
MID-CONTINENT SAMPLES
ILLINOIS BASIN SAMPLES
EASTERN SAMPLES
Anthracite and semianthracite
Bituminous (part?)
Low-volatile bituminous
Medium- and high-volatile bituminous
Subbituminous and lignite (part?)
Subbituminous
Lignite
Isolated occurrence of coal of unknown extent
A— Anthracite
B— Bituminous
S— Subbituminous
L— Lignite

Fig. 1 – Coal fields of conterminous United States showing regional designations used in the text.

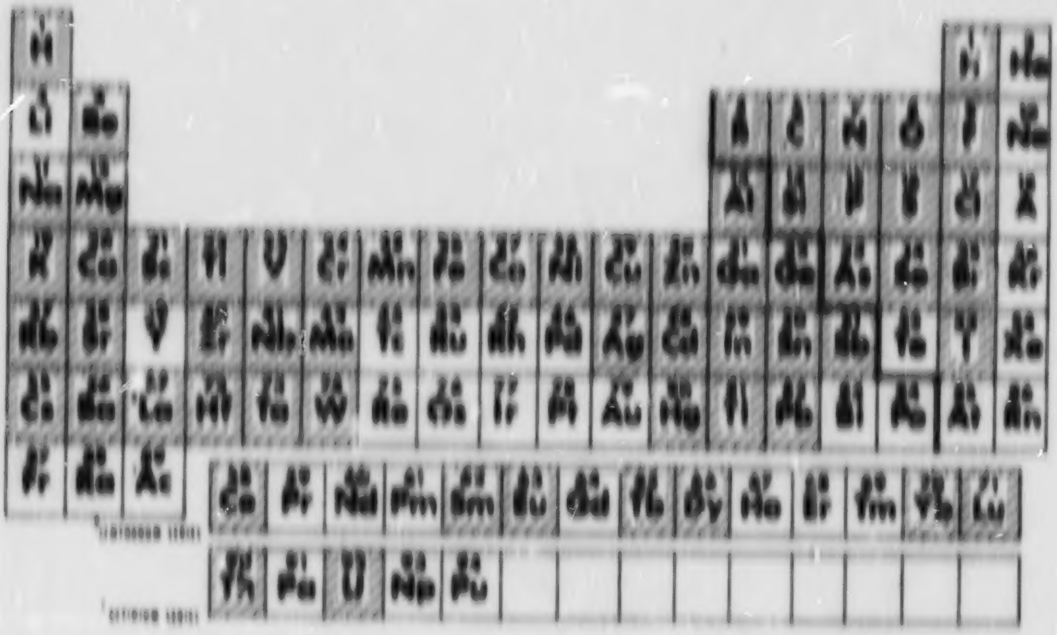

Fig. 2 - Elements reported in this study indicated by diagonal lines on the periodic table.

The present report includes data on analytical determinations made on 172 whole coal samples, 64 washed coal samples, and 40 bench samples. The 60 major, minor, and trace elements determined were aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), boron (B), bromine (Br), cadmium (Cd), calcium (Ca), carbon (C), cerium (Ce), cesium (Cs), chlorine (Cl), chromium (Cr), cobalt (Co), copper (Cu), dysprosium (Dy), europium (Eu), fluorine (F), gallium (Ga), germanium (Ge), gold (Au), hafnium (Hf), hydrogen (H), indium (In), iodine (I), iron (Fe), lanthanum (La), lead (Pb), lutetium (Lu), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), nitrogen (N), oxygen (O), phosphorus (P), potassium (K), rubidium (Rb), samarium (Sm), scandium (Sc), selenium (Se), silicon (Si), silver (Ag), sodium (Na), strontium (Sr), sulfur (S), tantalum (Ta), terbium (Tb), thallium (Tl), thorium (Th), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V), ytterbium (Yb), zinc (Zn), and zirconium (Zr) (fig. 2).

The following coal parameters were usually determined and are reported for most samples: moisture, low-temperature ash (mineral matter), high-temperature ash, total sulfur, sulfate sulfur, pyritic sulfur, organic sulfur, heating value (BTU), free swelling index (FSI), Gieseler plasticity, water-soluble chlorine, proximate analyses (volatile matter, fixed carbon), and ultimate analyses (C, H, N, O). In addition, during the project, useful techniques were developed for instrumental neutron activation analysis with a Ge(Li) detector (INAA) and for atomic absorption spectrometry (AA) using a graphite furnace excitation source (see appendix).

The appendix includes: 1) the techniques used to prepare the samples for chemical analyses; 2) the analytical methods developed for determination of many of the trace elements in coal; 3) a discussion of the results obtained by two or more analytical methods for the same element; and 4) summary tables listing the analytical techniques used in the determination of the elements reported in the body of the report.

The total amount of data in this report is very large—approximately 20,000 determinations. Complete geologic interpretation of these data is beyond the scope of this report. However, some partial statistical analyses of the chemical analytical data have been completed. For each element the data on whole coal samples have been analyzed statistically for arithmetic mean, geometric mean, range, and standard deviation. The data have also been tested for linear relationships among the elements, and a matrix of correlation coefficients is presented. Elemental concentrations of the coals analyzed have been compared to the average concentrations of the elements in the earth's crust (clarke values). Concentrations of elements in coals from the eastern and the western coal fields of the United States have been compared to concentrations of those elements in coals of the Illinois Basin. Chemical analytical data determined on bench samples have been analyzed similarly; the distribution of the elements in individual benches of a coal are shown as histograms on which the benches are scaled as to thickness and non-coal partings are shown.

An additional set of analytical values was determined on a series of "washed" coal samples. These samples were separated into specific gravity fractions and each fraction was analyzed for most of the same major, minor, and trace elements as were the whole coal samples. The results of the analyses of these samples are of special value for two reasons. First, the results demonstrate which of the elements can be removed from the coals by specific gravity techniques and the amount of each element that can be so removed. Second, such data can indicate the mode of occurrence of an element in the coal, whether it is in organic or in inorganic combination and, if in inorganic combination, can suggest with which group of minerals it is most likely to be associated.

A number of tables of data, all of which are computer generated, are included in this report. Table 1 lists all the abbreviations that were necessarily used in those tables, and thereby appreciably reduces the number of footnotes needed in the individual tables.

TABLE 1—ABBREVIATIONS USED IN TEXT AND TABLES

Å	angstrom unit
AA	Atomic absorption
ACS	American Chemical Society
ADL	Air-dry loss
ASTM	American Society for Testing and Materials
B	Bench sample
BCURA	British Coal Utilization Research Association
Btu	British Thermal Units
C	Column sample
CDC	Composite drill core sample
CFC	Composite face channel sample
CGB	Composite grab sample
cm	Centimeters
DC	Drill core sample
EPA	United States Environmental Protection Agency
F	Float fraction
FC	Face channel sample
FIXC	Fixed carbon
FS	Float-sink fraction
g	gamma
GB	Grab sample
Ge-Li	Lithium drifted germanium (detector)
HTA	High-temperature ash
HVAB	High volatile A bituminous
HVBB	High volatile B bituminous
HVCB	High volatile C bituminous
in	inch
INAA	Instrumental neutron Activation Analysis
ISE	Ion-Selective Electrode
kg	kilogram
LTA	Low-temperature ash
LVB	Low volatile bituminous
mg	milligram
ml	milliliter
MOIS	Moisture, as received
MVB	Medium volatile bituminous
NAA	Neutron Activation Analysis
NBS	National Bureau of Standards
OE-DR	Optical Emission-Direct Reading
OE-P	Optical Emission-Photographic
ORS	Organic sulfur
ppm	parts per million
PYS	Pyritic sulfur
RM	Run of mine sample
S	Sink fraction
SBA	Sub-bituminous - A
SBB	Sub-bituminous - B
SBC	Sub-bituminous - C
STD	Standard deviation
SUS	Sulfate sulfur
SXRF	Sulfur by X-ray Fluorescence
TOS	Total sulfur
u	micro-
USBM	United States Bureau of Mines
USGS	United States Geological Survey
VOL	Volatile matter
W	Washed sample
XRF	X-ray Fluorescence

TYPE AND SOURCE OF COAL SAMPLES

Chemical analyses of 172 whole coal samples were made for this study. One hundred thirty-five of the samples were face-channel or composite face-channel samples collected, in nearly all cases, in coal mines by Illinois State Geological Survey personnel. Each face-channel sample was cut by hand with a pick and represented the full height of the coal, excluding only mineral bands, partings, or nodules more than one centimeter (3/8 in.) thick. This procedure follows a longstanding practice at the Illinois State Geological Survey and is based on a technique described by Holmes (1911) in which mineral bands greater than three-eighths inch (1 cm) in thickness were excluded. Generally, three face-channel samples were collected in each mine, but in some mines less were collected because of local conditions. The face channel samples were crushed to pass a one-eighth inch (0.32 cm) screen, combined into a composite sample, and then riffled to the desired quantity.

The coal sample was comminuted further to 20 mesh (740 µm), 40 mesh (420 µm), 60 mesh (250 µm), 100 mesh (149 µm), or finer, depending on the analytical technique to be applied. In all cases, the sample was subdivided into aliquots by riffle-type sample splitters or by quartering the sample. The parts are considered representative of the original coal sample. Those samples ground between 20 mesh and 100 mesh were ground with a Pitchford Selective Particle Size Grinder. The grinder employed a reciprocating cylinder that was filled with steel balls and was continuously flushed with compressed air. Finer particle sizes were obtained by various other mechanical and hand methods (see appendix).

Table 2 is an index of all the whole coal samples reported upon in this study. For each coal the analysis number ("C" number), state or origin, bed name or other descriptive term, rank of the coal, and sample type are listed. We recognize the difficulty in analyzing data from coal samples of different types. Therefore, all samples are treated in as similar a manner as possible. For example, drill core samples (DC) were carefully described and mineral bands or partings over one centimeter thick were excluded, following the same procedure as for face-channel samples (FC and CFC). Run of mine samples (RM), a few samples of washed coals (W), and a few face channel samples were provided by coal companies and by state and federal agencies. We are grateful for the assistance of those companies and agencies and assume that the samples are representative of the coal produced at the mines that were sampled.

The coal analysis number, the letter "C" followed by five digits, is the single unique number assigned to a sample that has had any chemical analysis. It is the basis on which the samples are ordered in the data tables, thus it will be necessary to refer to table 2 for identification of those samples.

ANALYSES OF WHOLE COAL SAMPLES

Analytical Data:

The results of the chemical analyses of the 172 coal samples are given in tables 3 through 7. All analyses in this report are given on the "whole coal" basis and not as a percentage of ash. Table 3 lists the results of the analyses for 45 trace elements, all reported in parts per million (ppm). Table 4 shows the determinations of the major and minor elements on the same coals, reported in percent (%). The standard coal analyses (%), proximate (%), ultimate (%), and heating value (btu/lb), are given in tables 5 and 6. In addition, table 6 contains the low-temperature ash values as well as the high-temperature ash values for each coal, reported in percent (%). Table 7 contains the results of the analyses for varieties of sulfur and two total sulfur determinations, one by the standard ASTM method and the other by X-ray fluorescence spectroscopy. Analytical methods used in determining the reported values are given in the Appendix (table J).

Statistical Analyses of Data:

Analytical data from the whole coal samples were grouped by geographic origin of the samples (fig. 1). There were 114 samples from the Illinois Basin, 29 samples from the western coal-producing areas, and 23 samples from eastern United States (Appalachian coals). This total of 166 samples is six less than the number reported in tables 3 through 7. Two National Bureau of Standards (NBS) samples were omitted from the compilations, as were three samples from Iowa, and one sample from Missouri (western interior region). These last four were omitted because they do not by themselves constitute a valid statistical sampling of the Western Interior Basin. Recent publications that include many more data on coals from the western interior region are by Swanson et al., 1976; Hatch, Avcin, Wedge and Brady, 1976; and Wedge et al., 1976.

(Text continued on page 18)

Tables 3, 4, 5, 6, and 7 follow on pages 12 through 37. Samples are listed by sample number (for example, 015496). Identification of samples may be made by referring to table 2 on pages 8 and 9. Table 1 on page 6 lists abbreviations used in the tables.

TABLE 3—TRACE ELEMENTS IN WHOLE COAL SAMPLES
(parts per million, moisture-free, whole coal basis)

TABLE 3—Continued

NOTE: Samples listed by sample number (D-number). Refer to table 2 for identification of samples.

TABLE 3—Continued

TABLE 3—Continued

[illegible]

NOTE: Samples listed by sample number (C-number). Refer to table 2 for identification of samples.

TABLE 3—Continued

TABLE 3.--Continued

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NOTE: Samples listed by sample number (D-number). Refer to table 2 for identification of samples.

TABLE 3—Continued

TABLE 3—Continued

[illegible]

NOTE: Samples listed by sample number (C-number). Refer to table 2 for identification of samples.

TABLE 3—Continued

[illegible]

TABLE 3—Continued

NOTE: Samples listed by sample number (C-number). Refer to table 2 for identification of samples.

TABLE 3—Continued

TABLE 3—Continued

NOTE: Samples listed by sample number (D-number). Refer to table 2 for identification of samples.

TABLE 3—Continued

TABLE 3—Continued

NOTE: Samples listed by sample number (C-number). Refer to table 2 for identification of samples.

TABLE 3—Continued

TABLE 3—Concluded

SAMPLE	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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NOTE: Samples listed by sample number (D-number). Refer to table 1 for identification of samples.

TABLE 4--MAJOR AND MINOR ELEMENTS IN WHOLE COAL SAMPLES
(percent moisture-free whole coal basis)

SAMPLE	AL	CA	CL	FE	K	MG	NA	SI	TI
C12059	1.26	0.62	0.03	1.75	0.15	0.04	0.068	2.18	0.06
C12495	0.73	0.59	0.13	2.63	0.10	0.04	0.089	2.21	0.04
C12811	1.20	0.93	0.26	1.50	0.16	0.04	0.060	2.45	0.06
C12842	1.16	1.68	0.20	2.55	0.12	0.05	0.022	2.55	0.07
C13039	1.18	0.87	0.37	2.07	0.18	0.02	0.199	1.80	0.06
C13046	0.71	0.65	0.25	2.50	0.11	0.04	0.078	1.97	0.04
C13329	1.11	0.27	0.11	2.02	0.17	0.05	0.065	2.20	0.06
C13533	1.01	0.30	0.40	1.92	0.16	0.05	0.087	1.95	0.06
C13664	1.18	0.50	0.37	2.70	0.17	0.06	0.200	2.65	0.05
C13804	0.60	0.30	0.30	1.90	0.09	0.03	0.009	0.58	0.02
C13895	1.29	0.50	0.05	2.60	0.16	0.06	0.080	2.77	0.06
C13975	1.39	0.70	0.02	1.70	0.20	0.05	0.020	2.81	0.07
C13983	1.11	0.63	0.02	2.89	0.17	0.05	0.033	2.27	0.07
C14198	0.97	2.18	0.15	2.48	0.16	0.17	0.011	2.55	0.06
C14570	1.20	0.30	0.09	1.30	0.15	0.04	0.040	1.91	0.03
C14609	1.05	0.97	0.16	1.91	0.16	0.06	0.016	1.89	0.07
C14613	1.41	0.55	0.53	1.09	0.17	0.04	0.195	2.55	0.08
C14630	1.31	0.58	0.84	0.80	0.17	0.04	0.090	2.31	0.07
C14646	1.50	0.49	0.05	2.58	0.17	0.05	0.018	2.09	0.06
C14650	0.63	0.53	0.02	5.06	0.08	0.02	0.005	1.07	0.05
C14686	1.11	0.56	0.81	1.70	0.15	0.02	0.100	2.10	0.05
C14721	1.04	0.65	0.02	1.75	0.15	0.01	0.021	2.00	0.06
C14735	1.08	0.78	0.13	1.98	0.15	0.03	0.098	2.60	0.06
C14774	1.00	1.31	0.07	1.71	0.19	0.05	0.025	2.65	0.05
C14796	1.38	0.40	0.03	0.69	0.27	0.06	0.066	2.06	0.06
C14838	1.31	0.73	0.16	1.78	0.16	0.06	0.130	3.03	0.08
C14870	1.00	0.60	0.18	1.72	0.13	0.03	0.095	1.89	0.05
C14982	1.40	0.97	0.09	1.50	0.17	0.06	0.072	2.60	0.06
C15012	1.18	1.07	0.09	1.98	0.17	0.04	0.017	2.22	0.07
C15038	1.20	0.68	0.11	1.28	0.21	0.04	0.034	2.26	0.07
C15079	3.06	0.52	0.01	2.30	0.64	0.11	0.030	5.61	0.15
C15117	1.31	0.28	0.01	2.40	0.16	0.05	0.020	2.17	0.07
C15125	1.01	1.78	0.02	1.70	0.18	0.04	0.050	2.70	0.06
C15206	0.98	1.60	0.01	1.87	0.11	0.01	0.119	2.50	0.05
C15231	1.30	0.90	0.19	1.70	0.17	0.07	0.100	2.67	0.06
C15263	1.01	0.10	0.02	2.65	0.15	0.04	0.015	1.66	0.05
C15270	1.13	0.82	0.11	1.65	0.17	0.06	0.049	2.17	0.06
C15331	0.88	3.67	0.16	2.48	0.19	0.01	0.018	2.04	0.05
C15369	1.09	0.61	0.23	2.60	0.17	0.11	0.036	2.06	0.06
C15418	1.53	0.06	0.03	1.00	0.30	0.06	0.088	2.87	0.09
C15432	1.56	1.18	0.19	1.80	0.13	0.03	0.100	3.19	0.09
C15436	1.21	0.28	0.11	1.30	0.17	0.06	0.120	2.79	0.06
C15454	0.77	0.98	0.03	0.68	0.13	0.05	0.020	1.77	0.07
C15456	1.36	0.67	0.01	1.70	0.20	0.01	0.030	2.70	0.07

TABLE 4—Continued

SAMPLE	AL	CA	CL	FE	K	MG	NA	SI	TI
015496	1.08	0.52	0.02	1.92	0.15	0.04	0.018	2.21	0.06
015566	0.93	0.93	0.01	2.81	0.06	0.01	0.302	0.88	0.08
015678	0.66	1.02	0.02	3.00	0.04	0.03	0.030	0.94	0.08
015717	1.30	1.91	0.02	1.80	0.14	0.05	0.030	0.79	0.06
015791	1.50	0.41	0.52	1.36	0.20	0.06	0.180	0.76	0.07
015868	1.30	0.91	0.48	0.46	0.15	0.03	0.100	0.38	0.06
015872	1.65	1.32	0.01	2.00	0.16	0.09	0.080	0.72	0.07
015943	1.14	0.14	0.26	2.17	0.15	0.04	0.017	0.09	0.07
015944	1.20	0.14	0.31	2.19	0.18	0.04	0.010	0.04	0.07
015999	1.57	0.21	0.07	1.90	0.18	0.05	0.080	3.01	0.08
016030	1.23	0.21	0.17	2.10	0.23	0.06	0.080	0.47	0.07
016139	1.33	0.71	0.17	1.80	0.21	0.06	0.140	0.95	0.06
016264	0.92	0.56	0.01	2.05	0.16	0.04	0.051	1.90	0.05
016265	1.42	1.16	0.01	1.86	0.15	0.06	0.019	0.75	0.04
016317	1.14	0.73	0.11	1.70	0.12	0.05	0.080	0.58	0.07
016408	1.02	0.23	0.10	3.51	0.18	0.01	0.007	1.51	0.05
016501	1.30	0.72	0.43	1.99	0.13	0.04	0.119	0.64	0.06
016543	1.51	2.67	0.02	1.50	0.16	0.04	0.040	0.56	0.08
016564	1.06	0.37	0.03	2.87	0.14	0.14	0.037	0.80	0.08
016729	1.02	1.23	0.39	2.12	0.15	0.04	0.033	0.27	0.06
016741	1.40	1.09	0.12	1.60	0.17	0.09	0.080	0.64	0.07
016787	1.07	0.69	0.19	1.71	0.15	0.08	0.018	1.65	0.08
016919	1.34	0.14	0.15	1.65	0.24	0.04	0.018	0.36	0.08
016991	1.05	0.63	0.12	2.60	0.20	0.07	0.030	1.57	0.12
017001	0.86	5.82	0.27	2.76	0.15	0.02	0.048	2.08	0.06
017016	1.90	0.43	0.15	3.50	0.13	0.05	0.130	0.66	0.08
017085	1.76	1.44	0.01	0.69	0.06	0.09	0.027	1.11	0.08
017086	1.71	1.60	0.02	0.60	0.11	0.21	0.020	1.09	0.06
017087	1.63	1.59	0.01	1.23	0.14	0.25	0.019	1.10	0.06
017093	1.16	1.01	0.17	2.35	0.10	0.03	0.002	0.30	0.05
017096	0.63	0.60	0.03	0.51	0.08	0.03	0.013	1.90	0.13
017089	0.62	0.39	0.25	0.69	0.08	0.02	0.009	0.75	0.03
017092	1.16	0.87	0.37	2.32	0.12	0.02	0.061	1.80	0.36
017095	2.56	0.30	0.04	2.55	0.27	0.07	0.021	4.50	0.11
017096	0.72	0.93	0.03	0.46	0.02	0.03	0.200	1.99	0.06
017097	1.02	0.62	0.02	0.35	0.12	0.09	0.028	1.32	0.06
017098	2.56	0.35	0.07	1.06	0.12	0.06	0.030	1.36	0.15
017039	1.53	0.25	0.08	2.01	0.15	0.05	0.006	0.52	0.06
017216	1.91	0.69	0.02	2.17	0.20	0.07	0.018	1.11	0.10
017243	1.70	0.76	0.05	2.53	0.27	0.39	0.032	1.63	0.08
017244	1.61	0.30	0.02	1.79	0.29	0.05	0.036	1.20	0.10
017245	1.24	0.11	0.10	2.60	0.15	0.0	0.081	0.51	0.06
017246	1.16	0.11	0.19	0.94	0.15	0.	0.082	1.61	0.08

TABLE 4—Continued

SAMPLE	AL	CA	CL	FE	K	MG	NA	SI	TI
C17278	1.41	0.38	0.07	2.25	0.10	0.09	0.116	3.13	0.07
C17279	1.41	0.38	0.07	2.80	0.10	0.05	0.120	3.13	0.07
C17303	1.15	2.57	0.12	0.93	0.13	0.09	0.088	3.01	0.07
C17304	1.72	0.52	0.02	2.05	0.21	0.06	0.021	1.29	0.07
C17305	1.25	1.18	0.03	2.51	0.22	0.05	0.024	2.63	0.06
C17307	2.37	1.16	0.06	3.07	0.53	0.10	0.078	6.09	0.08
C17309	0.73	2.47	0.02	0.55	0.02	0.07	0.069	1.25	0.05
C17601	1.16	0.17	0.18	2.38	0.18	0.04	0.013	2.29	0.06
C17721	1.21	0.21	0.31	1.69	0.21	0.05	0.071	3.07	0.07
C17970	2.21	0.70	0.10	1.11	0.33	0.11	0.039	3.98	0.11
C17984	1.11	0.37	0.20	1.66	0.17	0.03	0.016	2.07	0.07
C17986	1.16	1.22	0.30	1.56	0.17	0.04	0.027	2.30	0.07
C18009	0.53	0.07	0.22	1.04	0.08	0.02	0.032	0.72	0.05
C18040	1.14	1.86	0.03	1.59	0.15	0.05	0.020	2.77	0.05
C18058	1.65	0.49	0.02	1.68	0.20	0.06	0.015	3.43	0.08
C18301	1.10	0.18	0.26	2.10	0.13	0.04	0.020	2.00	0.06
C18320	1.60	0.88	0.10	1.80	0.19	0.07	0.090	3.20	0.07
C18349	0.81	0.33	0.20	2.60	0.13	0.04	0.030	1.60	0.04
C18350	0.64	1.20	0.20	2.80	0.13	0.06	0.030	1.80	0.03
C181[illegible]1	1.00	2.04	0.05	1.90	0.21	0.06	0.030	2.10	0.05
C18355	0.93	0.21	0.14	1.20	0.12	0.05	0.020	1.80	0.05
C18368	1.40	0.62	0.26	1.60	0.20	0.06	0.040	2.90	0.07
C18389	1.00	0.31	0.02	2.30	0.15	0.04	0.010	1.20	0.05
C18792	1.00	0.07	0.02	1.70	0.18	0.05	0.020	2.20	0.06
C18395	0.93	1.10	0.07	1.40	0.17	0.05	0.030	1.90	0.06
C18398	1.20	0.80	0.22	2.10	0.17	0.05	0.020	2.10	0.05
C18431	1.70	0.13	0.02	1.30	0.25	0.07	0.020	2.70	0.58
C18805	0.94	0.42	0.03	2.10	0.15	0.04	0.010	1.40	0.05
C18807	1.10	0.21	0.05	1.60	0.16	0.05	0.030	1.40	0.06
C18808	2.20	0.47	0.01	1.70	0.52	0.11	0.080	4.40	0.10
C18811	1.10	0.32	0.07	2.30	0.16	0.05	0.010	2.10	0.06
C18815	1.20	0.42	0.01	1.90	0.18	0.05	0.020	2.00	0.06
C18819	2.00	0.25	0.03	2.00	0.28	0.10	0.030	4.70	0.09
C18821	1.30	0.77	0.26	1.80	0.27	0.07	0.150	2.80	0.06
C18833	0.65	2.00	0.02	0.60	0.01	0.26	0.420	1.00	0.04
C18836	0.31	2.00	0.01	0.60	0.03	0.18	0.370	0.58	0.02
C18837	0.47	2.90	0.03	0.40	0.07	0.22	0.460	0.99	0.03
C18840	0.89	1.70	0.02	0.50	0.03	0.21	0.330	1.30	0.02
C18881	0.52	2.80	0.02	0.40	0.03	0.28	0.100	0.71	0.02
C18884	0.73	3.80	0.01	0.50	0.01	0.39	0.020	1.10	0.05
C18885	0.19	2.10	0.02	0.30	0.01	0.19	0.010	1.33	0.05
C18886	0.42	1.50	0.02	0.30	0.0[illegible]	0.07	0.270	0.38	0.04
C18889	0.51	1.30	0.01	0.50	0.01	0.04	0.270	0.53	0.06

TABLE 4—Concluded

SAMPLE	AL	CA	CL	FE	K	MG	NA	SI	TI
C18550	0.59	1.80	0.01	0.30	0.01	0.12	0.600	0.95	0.05
C18551	0.52	1.50	0.00	0.40	0.03	0.10	0.160	0.69	0.05
C18554	0.70	0.66	0.06	0.40	0.01	0.09	0.100	1.60	0.06
C18557	0.36	3.31	0.02	0.30	0.02	0.12	0.010	0.71	0.02
C18558	0.60	2.00	0.03	0.50	0.05	0.13	0.010	0.66	0.04
C18562	1.50	2.99	0.01	0.70	0.10	0.13	0.010	2.30	0.10
C18563	2.00	1.30	0.02	1.00	0.32	0.20	0.040	4.70	0.07
C18565	1.60	3.40	0.02	0.40	0.10	0.17	0.010	3.10	0.07
C18566	1.10	3.10	0.03	1.20	0.07	0.15	0.010	2.10	0.05
C18493	1.40	0.91	0.15	2.50	0.16	0.06	0.100	2.70	0.07
C18560	1.40	0.51	0.05	2.60	0.13	0.06	0.040	3.20	0.06
C18572	0.86	2.70	0.01	2.70	0.07	0.05	0.020	1.50	0.03
C18573	1.70	0.63	0.02	3.70	0.20	0.07	0.030	3.60	0.05
C18574	0.90	2.20	0.02	3.20	0.10	0.05	0.020	1.60	0.03
C18581	2.60	0.12	0.17	2.00	0.56	0.07	0.020	4.00	0.11
C18590	1.20	0.28	0.16	1.90	0.26	0.05	0.060	3.10	0.07
C18594	0.94	0.60	0.13	1.90	0.16	0.04	0.070	2.10	0.07
C18664	1.10	0.29	0.04	2.30	0.17	0.05	0.020	2.20	0.07
C18685	0.76	0.01	0.04	2.00	0.10	0.03	0.020	1.30	0.03
C18689	0.93	0.66	0.04	1.50	0.12	0.04	0.030	1.70	0.06
C18693	0.99	0.56	0.03	2.60	0.16	0.05	0.040	1.90	0.03
C18697	1.10	0.16	0.03	2.00	0.12	0.05	0.010	2.10	0.06
C18701	1.06	0.27	0.02	1.90	0.16	0.05	0.020	1.90	0.07
C18816	1.50	0.63	0.01	0.60	0.03	0.10	0.023	1.90	0.07
C18820	1.40	0.56	0.74	0.90	0.21	0.06	0.070	2.50	0.12
C18824	2.00	0.10	0.01	0.70	0.12	0.03	0.020	3.00	0.12
C18825	1.90	0.09	0.06	2.26	0.46	0.07	0.030	3.10	0.09
C18829	2.10	0.23	0.06	2.40	0.42	0.09	0.030	2.90	3.06
C18830	1.90	0.34	0.17	0.90	0.23	0.36	0.040	2.10	0.06
C18831	1.20	0.69	0.27	1.20	0.06	0.06	0.010	1.00	0.05
C18832	1.30	0.30	0.23	1.20	0.26	0.06	0.020	2.10	0.06
C18833	2.30	0.27	0.16	0.90	0.40	0.08	0.070	2.90	0.11
C18837	2.10	0.15	0.02	1.40	0.36	0.06	0.040	3.10	0.14
C18841	1.20	0.53	0.60	1.70	0.16	0.04	0.060	2.30	0.06
C18844	1.20	0.55	0.13	1.10	0.13	0.04	0.030	1.90	0.06
C18846	1.90	0.35	0.02	0.70	0.26	0.05	0.030	2.60	0.13
C18849	3.10	0.42	0.01	1.60	0.66	0.15	0.060	5.30	0.16
C18853	1.10	0.65	0.10	1.60	0.09	0.04	0.060	1.60	0.06
C18857	1.10	0.58	0.07	2.20	0.17	0.05	0.100	2.60	0.06
C18992	1.20	0.80	0.03	0.90	0.07	0.07	0.170	2.40	0.07
C18993	0.72	0.74	0.13	0.90	0.01	0.07	0.040	0.38	0.04
C19000	1.40	0.46	0.12	0.80	0.02	0.07	0.150	0.71	0.06

TABLE 5—PROXIMATE ANALYSES OF WHOLE COAL SAMPLES
(percent of whole coal except for Btu values)

NOTE: See table 1 for abbreviations; see table 2 for identification of samples. All values are on a moisture-free whole coal basis except for air dry loss (ADL) and moisture (MOIST).

TABLE 6—ULTIMATE ANALYSES OF WHOLE COAL SAMPLES
[percent, moisture-free, whole coal basis]

NOTE: Refer to table 1 for abbreviations and to table 2 for identification of samples.

TABLE 7—SULFUR ANALYSES OF WHOLE COAL SAMPLES
(percent, moisture-free whole coal basis)

NOTE: Refer to table 1 for abbreviations and to table 2 for identification of samples.

As a first step in the statistical analyses of the data, geometric means, arithmetic means, standard deviations, and ranges (minimum and maximum values) were calculated for each of the analytical parameters. The results of these calculations are summarized in tables 8 through 10. Because determinations for all variables were not reported for all samples (see appendix), a missing-data statistical analysis computer program, adapted from Davis (1974) and IBM (1970), was used in this study. This computer program identified the missing data and omitted them when calculating the statistical values.

Trace element concentrations of Cd, Ge, I, In, Lu, Mo, P, Pb, Rb, Sn, Sr, and U were reported in some samples as "less-than" values. A less-than value represents the identification of the presence of an element in a particular sample at a concentration below the limit of quantitative accuracy but above zero. The effect of these less-than values on the statistical parameters shown in tables 8 through 10 was discussed in a previous publication (Ruch et al., 1974, p. 16). It was concluded that the differences in mean values calculated in three different ways, 1) using the less-than value as an accepted value, 2) using one-half the less-than value, or 3) using zero, had little effect on the statistics except in those cases where the less-than values were a major proportion of the total sample population. The statistics reported in tables 8 through 10 are calculated by using the reported less-than value as the "true value" (<0.3 equal to 0.3). Summary statistics are not shown for those cases where the less-than values compose a significant part of the total population (for example Sn in all samples and Cd in samples from the eastern and the western United States).

Histograms of the distribution of trace, minor, and major elements and of the high-temperature and low-temperature ashes are given in figures 3 through 62. The data for 165 of the 172 coal samples are plotted on the histograms (omitting a weathered coal sample C17089, the two NBS samples, and the four samples from Iowa and Missouri) so that the three geographic groups may be differentiated. The data from the Illinois Basin coals are plotted as vertically striped bars, those from the western United States as horizontally striped bars, and those from the eastern United States as unpatterned bars. The horizontal axis is divided into class intervals and the vertical axis represents the number of samples in each class. Those samples whose values are beyond the last regular class interval are plotted following a break in the abscissa and are identified with a plus sign (+).

Geometric means are included in tables 8, 9, and 10 and are used to compare data from the three regions. The geometric mean was calculated by taking the logarithm of each analytical value, summing the logarithms, dividing the sum by the total number of values and obtaining the antilogarithm of the result. The arithmetic mean was calculated by summing the data and dividing the sum by the number of samples. For comparison of samples, geometric means are preferred to arithmetic means because the extremely high values (often the result of epigenetic mineralization within the coal) are less of an influence on the geometric mean value than on the arithmetic mean. Therefore, the geometric mean more closely approximates the value that would be expected in an unknown sample (Swanson et al., 1976; Miesch, 1967; Davis, 1974; and McCammon, 1975).

From the statistical analyses of the data shown on tables 8, 9, and 10 a number of interesting observations can be made. However, caution is necessary in making interpretations based on tables 9 and 10. Only 23 samples from the eastern United States made up the total population on table 9, and only 29 samples from the western United States made up the total population on table 10. Tables 9 and 10 are included so that they may be compared with the much larger population of 114 samples from the Illinois Basin that were used to prepare table 8. Several of these observations follow:

> 1. In coals from the Illinois Basin, elements that have relatively large ranges and standard deviations larger than their arithmetic means include As, Ba, Cd, I, Pb, Sb, and Zn. The standard deviation for Sb is also larger than the mean for Sb in both the eastern and western coals analyzed. Several of these elements have been identified in the sulfide fraction of the mineral matter. The mineral sphalerite contains Zn and Cd, galena contains Pb, some pyrites contain As and perhaps Sb, and Ba has been identified within the mineral barite. Data obtained from the determinations of these elements generally present a skewed pattern as can be seen in histograms of their distributions (figures 4, 6, 9, 22, 30, 32 and 46).
>
> 2. In coals from the Illinois Basin, elements that have relatively narrow ranges and standard deviations less than one-half the arithmetic mean include B, Be, Ga, F, Se, V, Ni, Al, Fe, Si, Ti, K, Mg and many of the rare earth elements. This list of elements includes those generally thought to be, at least in part, in organic combination and those elements that occur in the silicate minerals. These elements display a more or less normal distribution of analytical values (figs. 5, 7, 18, 17, 34, 43, 28, 48, 51, 56, 52 and 53).
>
> 3. In general, elemental concentrations tend to be highest in coals from the Appalachian Basin (eastern samples), lowest in coals from the western United States (western samples) and intermediate in amount in coals from the Illinois Basin. This is true with the following

elements: As, Ce, Co, Cr, Cs, Cu, Dy, Eu, F, Ga, Hg, I, In, La, Lu, Rb, Sb, Sc, Se, Sm, V, Yb, Al, Cl, S, and Ti.

4. Western coals sampled have the highest concentrations (maximum geometric mean values) for only five of the elements determined, Ba, P, Sr, Ca, and Na.

5. Coals from the Illinois Basin have the highest concentrations (maximum geometric mean values) of B, Be, Br, Cd, Ge, Mn, Ni, Pb, Zn, Fe, and S.

Coefficients resulting from the correlation of each parameter with every other parameter in coals from the Illinois Basin (114 samples) are given in Table 11. Several geochemical associations are apparent in these correlation coefficients and although most of them were mentioned by Ruch et al., 1974, they are repeated here.

1. The highest value of a positive correlation coefficient is for Zn and Cd (0.94 for coals of the Illinois Basin). Zinc occurs in coals of the Illinois Basin in the mineral sphalerite (ZnS) (Gluskoter et al., 1973; and Hatch, Gluskoter, and Lindahl, 1976). Cadmium is found in solid solution in the sphalerite in concentrations as high as 65 ppm (Gluskoter and Lindahl, 1973; and Hatch, Gluskoter, and Lindahl, 1976). The sphalerite in coal is epigenetically deposited along cleats and in clastic clay dikes (Cobb and Russell, 1976). Barium, which occurs as the mineral barite ($BaSO_4$), is also closely correlated with zinc and cadmium. The occurrence of barite in amounts large enough to be identified with the sphalerite in the coals has only been observed in a few instances. However, there does seem to be a geographical and statistical correlation between Ba and the cations in sphalerite, which suggests a common control of their deposition. The correlation coefficient of Ba:Zn is 0.72 and Ba:Cd is 0.87.

2. The elements of the following group have positive correlations with each other: As, Co, Ni, Pb, and Sb. These elements are commonly found in nature as sulfides and are included among the chalcophile elements (elements which have a strong affinity for sulfur). Germanium is positively correlated with many chalcophile elements in the Illinois Basin coals.

3. The elements classified as lithophile, which generally occur in the earth's crust as alumino-silicate minerals, have mutually positive correlations in coals. These elements are Si, Ti, Al, and K. A positive correlation of Mg with the lithophile elements also exists, but these correlations are not as strong as those between the above four elements.

4. There is a positive correlation of 0.65 between Mn and Ca; in coals of the Illinois Basin, Mn does not correlate as well with any other element. Manganese commonly substitutes for Ca in calcite ($CaCO_3$) and is presumed to be in that combination in coals.

5. Sodium and Cl have a positive correlation of 0.48 in the Illinois Basin samples. A similar correlation between chlorine and total alkalies was reported by Gluskoter and Rees (1964) and, in part, the correlation can be attributed to the deposition of Na and Cl in coals by saline ground water (Gluskoter, 1965a; and Gluskoter and Ruch, 1971).

6. Many of the rare earth elements have high positive correlations with other rare earth elements. This may be real, a result of the chemical similarity of these elements, or the correlation may, in part, be an artifact of the analyses.

(Text continued on page 69)

TABLE 8--MEAN ANALYTICAL VALUES FOR 114 WHOLE COAL SAMPLES FROM THE ILLINOIS BASIN COAL FIELD

Element	Arithmetic Mean		Geometric Mean		Minimum	Maximum	Standard Deviation	Number Samples	Number Less Than Values
AU	0.03	ppm	0.03	ppm	0.02	0.08	0.02	37	
AS	18	ppm	7.5	ppm	1.0	180	20	113	
B	112	ppm	95	ppm	12	230	50	99	
BA	100	ppm	75	ppm	5.0	750	110	99	
BE	1.7	ppm	1.5	ppm	0.5	4.0	0.82	113	
BR	12	ppm	10	ppm	0.6	52	7.5	113	
CD	2.2	ppm	0.59	ppm	0.1	65	7.6	113	
CE	15	ppm	12	ppm	2.4	50	7.5	98	41
CO	7.3	ppm	6.0	ppm	2.0	25	3.7	113	
CR	16	ppm	16	ppm	4.0	60	9.2	113	
CS	1.5	ppm	1.2	ppm	0.5	4.6	0.74	98	
CU	19	ppm	17	ppm	5.0	47	[illegible]	113	
DY	1.1	ppm	1.0	ppm	[illegible]	[illegible]	0.51	98	
EU	0.26	ppm	0.25	ppm	0.1	0.87	0.12	98	
F	67	ppm	61	ppm	27	150	25	113	
GA	3.2	ppm	3.0	ppm	0.8	10	1.2	113	
GE	6.9	ppm	4.8	ppm	1.0	47	6.5	113	11
HF	0.54	ppm	0.49	ppm	0.13	1.5	0.25	95	
HG	0.2	ppm	0.16	ppm	0.03	1.6	0.19	111	
[illegible]	1.7	ppm	1.0	ppm	0.29	15	2.0	98	12
[illegible]	0.16	ppm	0.13	ppm	0.01	0.53	0.11	98	8
LA	6.0	ppm	5.4	ppm	2.7	20	2.6	98	
LU	0.09	ppm	0.05	ppm	0.02	0.44	[illegible]	98	3
MN	53	ppm	40	ppm	[illegible]	210	41	113	
MO	8.1	ppm	5.7	ppm	[illegible]	29	6.4	111	6
[illegible]	21	ppm	19	ppm	1.6	60	10	113	
[illegible]	65	ppm	50	ppm	14	250	60	113	7
[illegible]	32	ppm	15	ppm	[illegible]	220	42	113	6
[illegible]	19	ppm	17	ppm	2.0	45	[illegible]	113	1
[illegible]	1.3	ppm	0.81	ppm	[illegible]	[illegible]	1.3	98	
[illegible]	2.7	ppm	2.5	ppm	1.2	7.7	1.1	113	
[illegible]	2.8	ppm	2.0	ppm	0.5	7.7	1.1	98	
[illegible]	[illegible]	ppm	1.1	ppm	0.5	[illegible]	1.0	113	
[illegible]	3.8	ppm	0.99	ppm	0.2	51	[illegible]	98	
[illegible]	45	ppm	40	ppm	10	130	8.8	60	52
[illegible]	0.15	ppm	0.14	ppm	0.07	0.3	23	98	9
[illegible]	0.22	ppm	0.16	ppm	0.05	0.69	0.08	58	
[illegible]	[illegible]		[illegible]		[illegible]	[illegible]	0.15	41	

TABLE 5—Continued

Element	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Standard Deviation	Number Samples	Number Less Than Value*
TH	2.1 ppm	1.9 ppm	0.71	5.1	0.87	98	
TL	0.65 ppm	0.59 ppm	0.12	1.3	0.31	63	
U	1.5 ppm	1.3 ppm	0.31	6.8	0.93	98	1
V	32 ppm	29 ppm	11	90	11	113	
W	0.88 ppm	0.63 ppm	0.05	5.1	0.89	98	
YB	0.58 ppm	0.53 ppm	0.27	1.6	0.21	98	
ZN	250 ppm	87 ppm	12	5300	650	113	
ZR	41 ppm	41 ppm	12	130	27	88	
AL	1.2 %	1.2 %	0.53	3.0	0.38	113	
CA	0.67 %	0.51 %	0.07	2.7	0.66	113	
CL	0.10 %	0.08 %	0.01	0.54	0.13	113	
FE	2.0 %	1.9 %	0.49	5.1	0.83	113	
K	0.17 %	0.16 %	0.06	0.58	0.07	113	
MG	0.05 %	0.05 %	0.01	0.17	0.02	113	
NA	0.05 %	0.03 %		0.2	0.04	113	
SI	2.4 %	2.3 %	0.88	5.7	0.7	113	
TI	0.06 %	0.06 %	0.02	0.15	0.02	113	
ADL	7.2 %	6.4 %	1.5	17	3.4	98	
MOIS	9.6 %	9.1 %	3.6	18	3.3	110	
VOL	40 %	40 %	27	46	3.1	111	
FIXC	49 %	49 %	41	61	3.6	111	
ASH	11 %	11 %	5.6	21	2.9	110	
BTU/LB	12712	12706	11512	14382	470	107	
C	70 %	70 %	62	80	3.0	110	
H	5.0 %	5.0 %	4.2	5.8	0.31	110	
N	1.3 %	1.3 %	0.73	1.8	0.18	110	
O	8.2 %	8.0 %	4.2	14	1.8	109	
HTA	11 %	11 %	3.3	20	2.6	112	
LTA	15 %	15 %	3.8	25	3.3	110	
ORS	1.8 %	1.8 %	0.37	3.2	0.6	110	
PYS	2.0 %	1.8 %	0.29	5.5	0.79	111	
SUS	0.1 %	0.05 %	0.01	1.1	0.18	109	
TOS	3.9 %	3.8 %	0.96	6.8	1.1	113	
SXRF	3.8 %	3.7 %	0.79	6.5	1.1	110	

TABLE 9—MEAN ANALYTICAL VALUES FOR 23 WHOLE COAL SAMPLES FROM THE EASTERN UNITED STATES (Appalachian coal fields)

Element	Arithmetic Mean		Geometric Mean		Minimum	Maximum	Standard Deviation	Number Samples	Number Less Than Values
AG	0.02	ppm	0.02	ppm	0.01	0.05	0.01	11	
AS	23	ppm	11	ppm	1.8	100	27	23	
B	52	ppm	25	ppm	6.0	120	37	23	
BA	200	ppm	170	ppm	72	590	110	16	
BE	1.3	ppm	1.1	ppm	0.23	2.5	0.56	23	
BR	12	ppm	8.9	ppm	0.77	25	7.6	23	
CD	0.25	ppm	0.19	ppm	0.10	0.60	0.18	23	21
CE	25	ppm	23	ppm	11	52	9.1	16	
CO	5.8	ppm	7.6	ppm	1.5	13	7.0	23	
CR	20	ppm	16	ppm	10	60	15	23	
CS	2.5	ppm	1.8	ppm	0.60	6.2	1.6	16	
CU	18	ppm	16	ppm	5.1	30	7.3	23	
DY	2.3	ppm	2.0	ppm	0.75	5.5	0.93	16	
EU	0.52	ppm	0.47	ppm	0.15	0.98	0.22	16	
F	89	ppm	85	ppm	50	150	27	23	
GA	5.7	ppm	5.2	ppm	2.9	11	2.6	23	
GE	1.5	ppm	0.87	ppm	0.10	6.0	1.7	23	9
HF	1.2	ppm	1.1	ppm	0.38	2.2	0.43	16	
HG	0.20	ppm	0.17	ppm	0.05	0.67	0.12	23	1
LI	1.7	ppm	1.8	ppm	0.33	4.9	1.1	16	1
[illegible]	0.24	ppm	0.22	ppm	0.13	0.37	0.08	16	
LA	15	ppm	13	ppm	5.1	27	5.3	16	
LU	0.22	ppm	0.18	ppm	0.05	0.40	0.12	16	
MN	18	ppm	12	ppm	2.6	61	15	23	
MO	5.6	ppm	1.9	ppm	0.10	22	5.3	23	1
NI	15	ppm	13	ppm	5.3	25	5.7	23	
P	150	ppm	81	ppm	15	1500	300	23	
PB	5.9	ppm	5.7	ppm	1.0	18	3.6	23	1
RB	20	ppm	17	ppm	9.0	63	13	16	
SB	1.5	ppm	1.1	ppm	0.25	7.3	1.2	23	
SC	5.1	ppm	5.0	ppm	1.6	8.3	1.8	16	
SE	3.0	ppm	2.9	ppm	1.1	6.3	1.0	23	
SM	2.6	ppm	2.5	ppm	0.87	5.3	0.98	16	
SN	2.0	ppm	0.97	ppm	0.20	9.0	2.4	16	7
SR	130	ppm	100	ppm	20	550	130	16	
TA	0.33	ppm	0.29	ppm	0.12	1.1	0.26	16	
TB	0.35	ppm	0.28	ppm	0.05	0.73	0.17	16	

TABLE 9—Continued

Element	Arithmetic Mean		Geometric Mean		Minimum	Maximum	Standard Deviation	Number Samples	Number Less Than Values
Sn	5.5	ppm	5.0	ppm	1.5	9.0	2.1	16	
Th									
U	1.5	ppm	1.3	ppm	0.50	2.9	0.73	11	
V	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	
W	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	
Yb	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	
Zn	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	
Zr	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	
AL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
CA	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
CL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
FE	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
K	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
MG	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
NA	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
SI	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
TI	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
ADL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
MOIS	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
VOL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
FIXC	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
ASH	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
BTU/LB	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	
C	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
H	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
N	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
O	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
HTA	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
LTA	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	

TABLE 10--MEAN ANALYTICAL VALUES FOR 28 WHOLE COAL SAMPLES FROM THE WESTERN UNITED STATES

Element	Arithmetic Mean	Geometric Mean	Minimum	Maximum	Standard Deviation	Number Samples	Number Less Than Values
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 10—Continued

Element	Arithmetic Mean		Geometric Mean		Minimum	Maximum	Standard Deviation	Number Samples	Number Less Than Values
TH	2.3	ppm	1.8	ppm	0.60	5.7	1.5	22	
TL									
U	1.0	ppm	0.80	ppm	0.30	2.5	0.65	22	5
V	16	ppm	12	ppm	5.6	53	12	[illegible]	
W	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	
YB	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	
ZN	[illegible]	ppm	[illegible]	ppm	[illegible]	[illegible]	[illegible]	[illegible]	1
ZR	[illegible]	ppm	[illegible]	ppm	[illegible]	170	[illegible]	[illegible]	
AL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
CA	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
FE	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
K	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
MG	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
NA	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
SI	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
TI	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
ADL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
MOIS	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
VOL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
FIXC	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
ASH	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
BTU/LB	[illegible]		[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	
C	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
H	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
N	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
O	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
ORG	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
PYR	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
SUL	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
TOS	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	%	[illegible]	%	[illegible]	[illegible]	[illegible]	[illegible]	

TABLE 11—
LINEAR REGRESSION (LEAST SQUARE) CORRELATION COEFFICIENTS OF ANALYTICAL DETERMINATION ON 114 COAL SAMPLES FROM THE ILLINOIS BASIN COAL FIELD

TABLE 11—Continued

TABLE 11—Continued

TABLE 11—Continued

[illegible]

TABLE 11—Continued

	SC	SE	SM	SN	SR	TA	TB	TH	TL	U	V	W	YB	ZN	ZR

TABLE 11—Continued

TABLE 11--Continued

	AL	CA	CL	FE	K	MG	NA	SI	TI	ADL	MOIS	VOL	FIXC	ASH	BTU
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 11—Continued

	AL	CA	CL	FE	K	MG	NA	SI	TI	AGL	MOIS	VOL	FIXC	ASH	BTU
AS	0.04	0.21	-0.15	-0.05	-0.08	-0.05	-0.07	-0.01	0.05	0.08	0.25	0.15	-0.11	-0.01	-0.06
LP	0.11	0.06	0.12	0.13	0.09	0.05	0.17	0.15	0.12	0.09	0.05	-0.09	0.01	0.09	-0.02
AL	1.00	-0.10	-0.13	-0.11	0.85	0.88	0.09	0.76	0.77	0.15	0.11	-0.30	-0.06	0.58	-0.56
CA	-0.10	1.00	-0.07	-0.11	-0.21	0.13	0.05	0.09	-0.11	0.11	0.16	0.12	-0.29	0.30	-0.25
CL	-0.13	-0.07	1.00	-0.26	-0.09	-0.18	0.58	-0.13	-0.07	-0.29	-0.27	-0.38	0.51	-0.19	0.37
FE	-0.11	-0.11	-0.26	1.00	-0.21	0.10	-0.19	-0.10	-0.12	0.07	-0.13	0.28	-0.38	0.17	-0.07
K	0.85	-0.21	-0.09	-0.21	1.00	0.83	0.01	0.68	0.68	-0.18	-0.16	-0.50	0.10	0.50	-0.37
MG	0.88	0.13	-0.18	0.02	0.83	1.00	-0.01	0.58	0.55	-0.06	-0.05	-0.26	-0.08	0.57	-0.38
NA	0.09	0.05	0.58	-0.19	0.01	-0.01	1.00	0.27	0.08	0.27	0.25	0.17	-0.25	0.15	-0.28
SI	0.76	0.09	-0.13	-0.10	0.68	0.58	0.27	1.00	0.76	0.12	0.10	-0.21	-0.25	0.70	-0.72
TI	0.77	-0.11	-0.07	-0.12	0.68	0.55	0.08	0.76	1.00	0.11	0.07	-0.50	0.10	0.80	-0.61
AGL	0.15	0.11	-0.29	0.07	-0.18	-0.06	0.27	0.12	0.11	1.00	0.82	0.50	-0.36	0.08	-0.38
MOIS	0.11	0.16	-0.27	-0.13	-0.16	-0.05	0.25	0.10	0.07	0.82	1.00	0.55	-0.35	-0.05	-0.32
VOL	-0.30	0.12	-0.38	0.28	-0.50	-0.26	0.12	-0.21	-0.50	0.50	0.55	1.00	-0.77	-0.12	-0.15
FIXC	-0.06	-0.29	0.51	-0.38	0.10	-0.08	-0.25	-0.25	0.10	-0.36	-0.35	-0.77	1.00	-0.55	0.67
ASH	0.58	0.30	-0.19	0.17	0.50	0.57	0.15	0.70	0.80	0.08	-0.05	-0.12	-0.55	1.00	-0.93
BTU	-0.56	-0.25	0.37	-0.07	-0.37	-0.38	-0.28	-0.72	-0.61	-0.38	-0.32	-0.15	0.67	-0.93	1.00
C	-0.33	-0.15	0.35	-0.25	-0.26	-0.35	-0.28	-0.59	-0.25	-0.33	-0.26	-0.27	0.60	-0.75	0.91
H	-0.28	-0.10	-0.01	0.03	-0.28	-0.19	-0.05	-0.51	-0.31	-0.05	-0.16	0.25	0.08	-0.51	0.38
N	-0.08	-0.13	0.61	-0.17	-0.07	-0.16	-0.01	-0.15	0.08	-0.31	-0.20	-0.32	0.59	-0.33	0.61
O	0.30	-0.12	[illegible]	-0.10	0.17	0.09	0.30	0.30	0.25	0.61	0.35	0.09	-0.60	0.08	-0.29
HTA	0.50	0.20	-0.21	0.22	0.52	0.92	0.17	0.73	0.55	0.06	-0.05	-0.12	-0.53	1.00	-0.89
LTA	0.37	0.27	-0.30	0.52	0.31	0.37	0.11	0.66	0.32	0.15	0.06	0.03	-0.56	0.81	-0.73
ORG	0.06	0.16	-0.42	0.31	-0.19	0.09	0.16	0.16	-0.13	0.33	0.32	0.67	-0.75	0.25	-0.56
PYR	-0.23	-0.09	-0.19	0.72	-0.21	-0.07	-0.22	-0.22	-0.35	-0.11	-0.05	0.20	-0.37	0.30	-0.19
SUL	0.05	-0.01	-0.09	0.15	0.17	0.16	0.08	0.16	0.15	-0.08	-0.15	-0.02	-0.07	0.21	-0.30
TSU	-0.12	0.05	-0.37	0.70	-0.19	0.05	-0.02	0.00	-0.25	0.10	-0.03	0.59	-0.56	0.38	-0.38
SRRF	-0.15	0.05	-0.41	0.62	-0.21	0.05	0.02	-0.03	-0.30	0.15	0.04	0.58	-0.60	0.29	-0.33

TABLE 11—Continued

	T	H	B	C	HTA	LTA	HRS	PTS	AUS	TUS	RERF
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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TABLE 11—Concluded

	C	H	N	O	HTA	LTA	ORS	PYS	SUS	TOS	[illegible]
SR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ZR	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
AL	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CL	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
FE	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
K	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
MG	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
NA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
SI	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
TI	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ADL	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
MOIS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
VOL	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
FIXC	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ASH	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
BTU	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H	[illegible]	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
O	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
HTA	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
LTA	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ORS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]	[illegible]
PYS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]	[illegible]
SUS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]	[illegible]
TOS	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00

Figures 3-62

In figures 3 through 62, the data from the eastern United States are plotted as unpatterned bars, those from the Illinois Basin as vertically striped bars, and those from the western United States as horizontally striped bars.

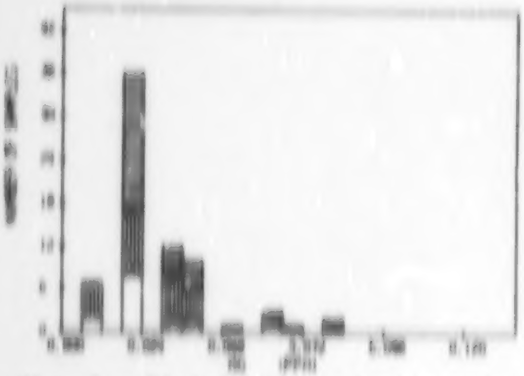

Fig. 3 - Distribution of silver in coals analysed.

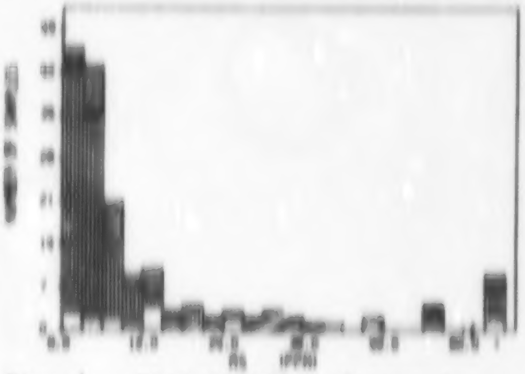

Fig. 4 - Distribution of arsenic in coals analysed.

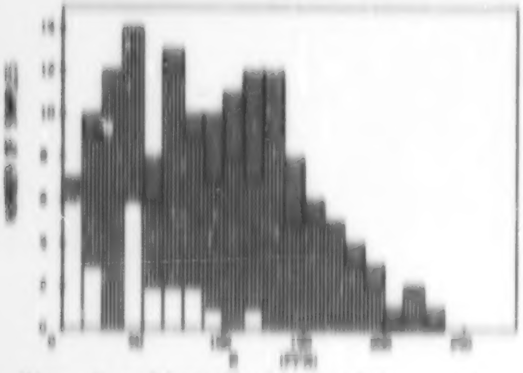

Fig. 5 - Distribution of boron in coals analysed.

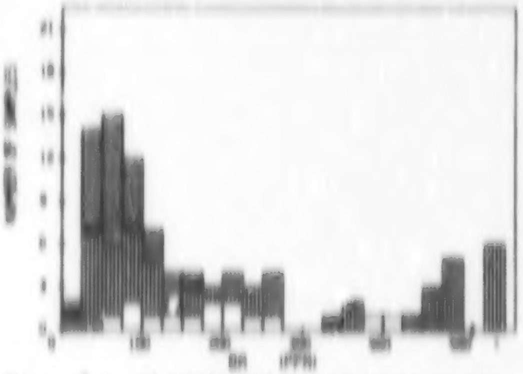

Fig. 6 - Distribution of barium in coals analysed.

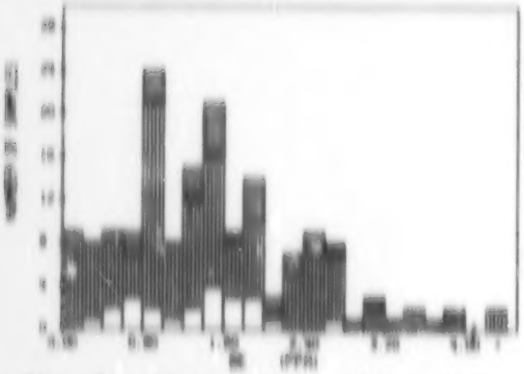

Fig. 7 - Distribution of beryllium in coals analysed.

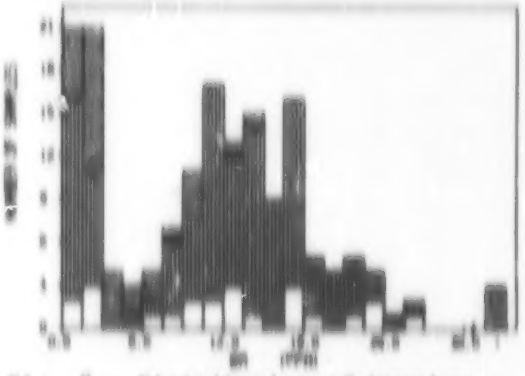

Fig. 8 - Distribution of bromine in coals analysed.

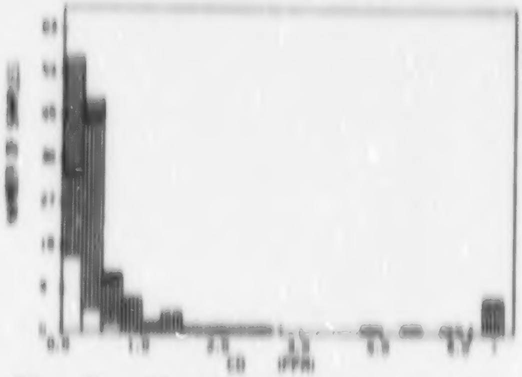

Fig. 9 - Distribution of cadmium in coals analysed.

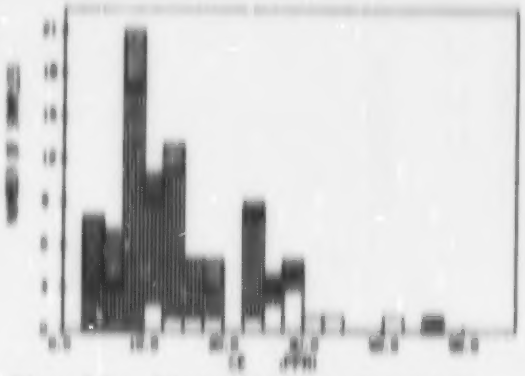

Fig. 10 - Distribution of cerium in coals analysed.

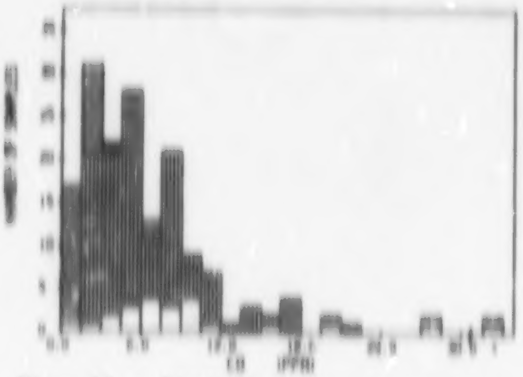

Fig. 11 - Distribution of cobalt in coals analysed.

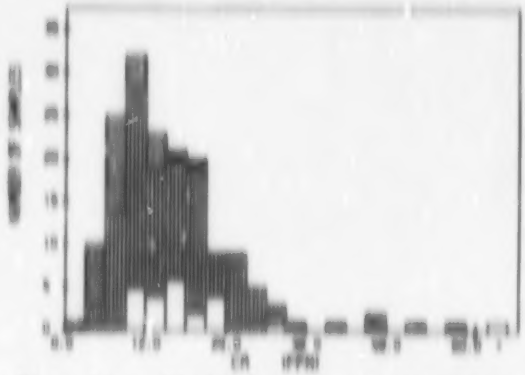

Fig. 12 - Distribution of chromium in coals analysed.

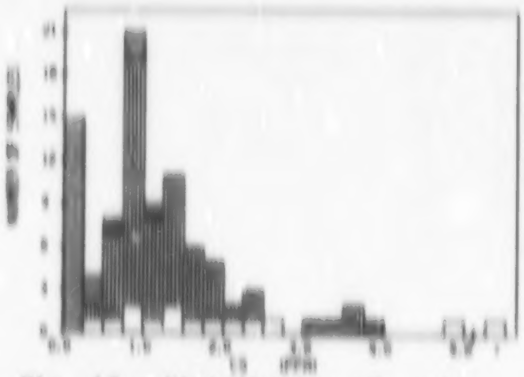

Fig. 13 - Distribution of cesium in coals analysed.

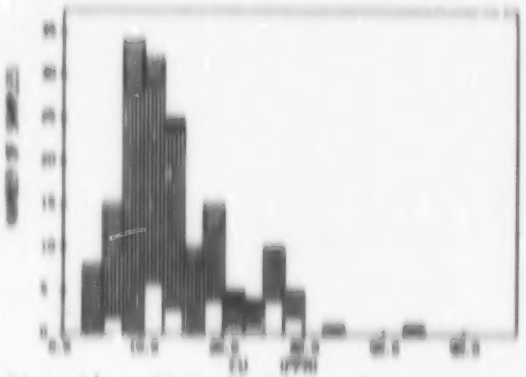

Fig. 14 - Distribution of copper in coals analysed.

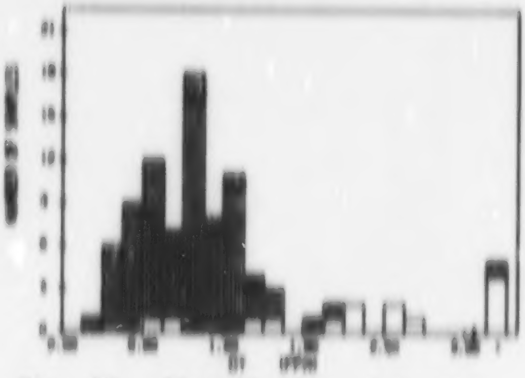

Fig. 15 – Distribution of dysprosium in coals analysed.

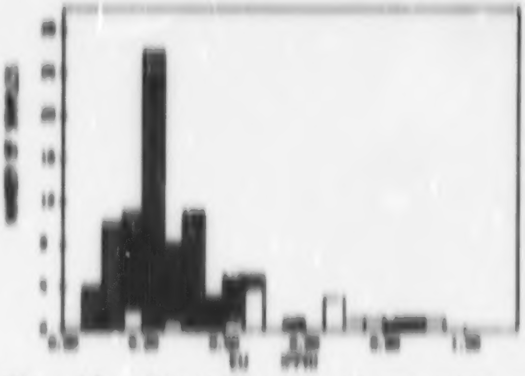

Fig. 16 – Distribution of europium in coals analysed.

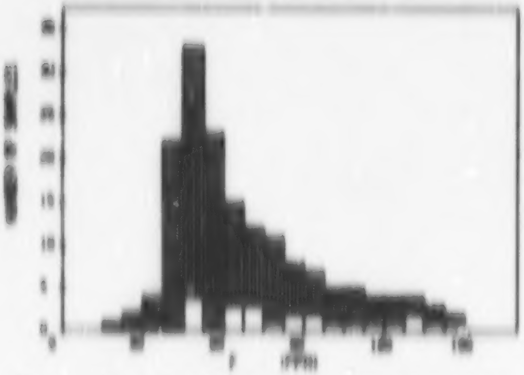

Fig. 17 – Distribution of fluorine in coals analysed.

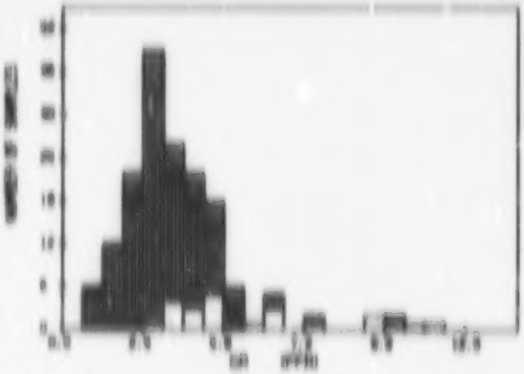

Fig. 18 – Distribution of gallium in coals analysed.

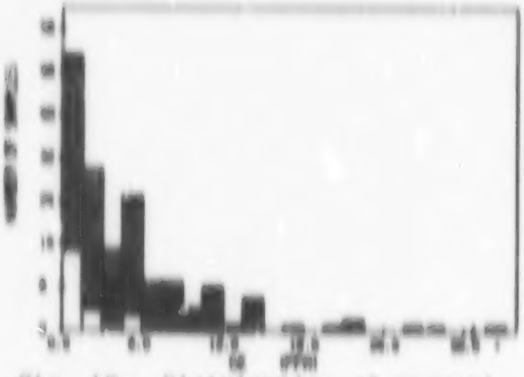

Fig. 19 – Distribution of germanium in coals analysed.

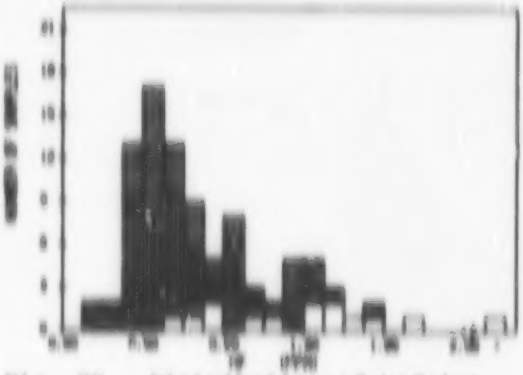

Fig. 20 – Distribution of hafnium in coals analysed.

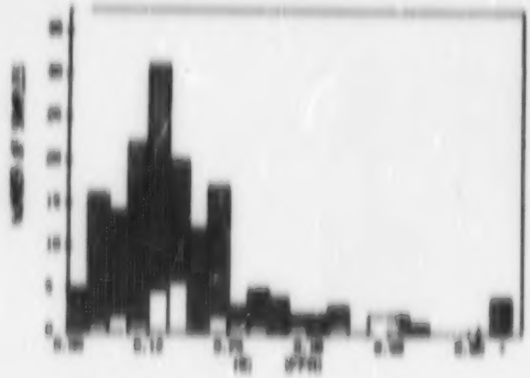

Fig. 21 - Distribution of mercury in coals analysed.

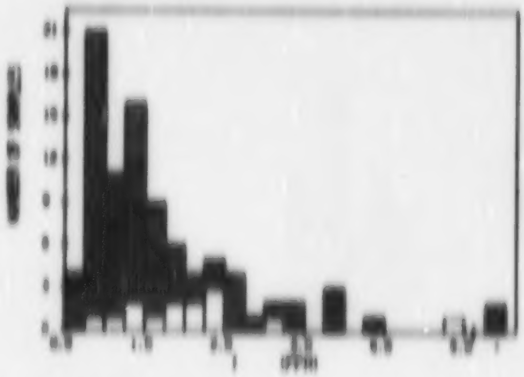

Fig. 22 - Distribution of iodine in coals analysed.

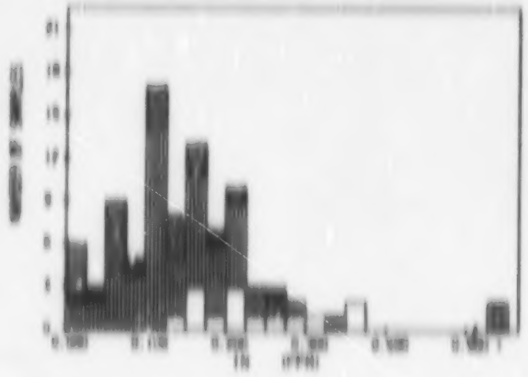

Fig. 23 - Distribution of indium in coals analysed.

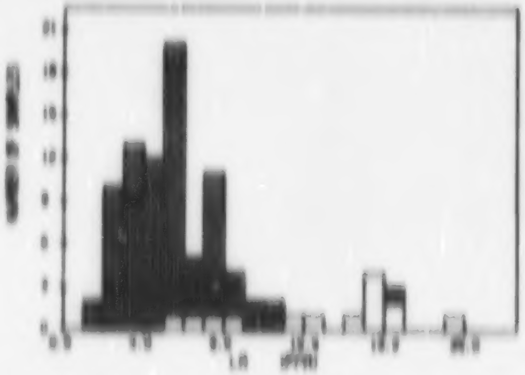

Fig. 24 - Distribution of lanthanum in coals analysed.

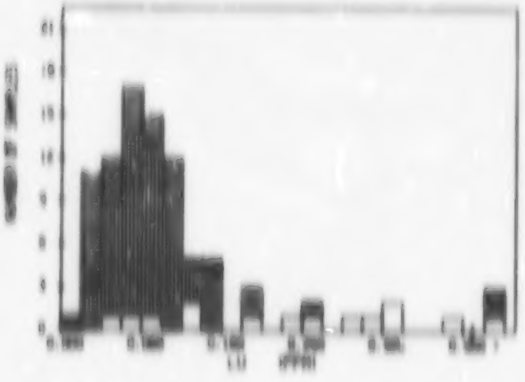

Fig. 25 - Distribution of lutetium in coals analysed.

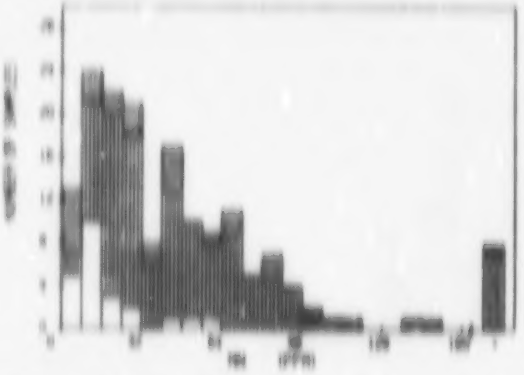

Fig. 26 - Distribution of manganese in coals analysed.

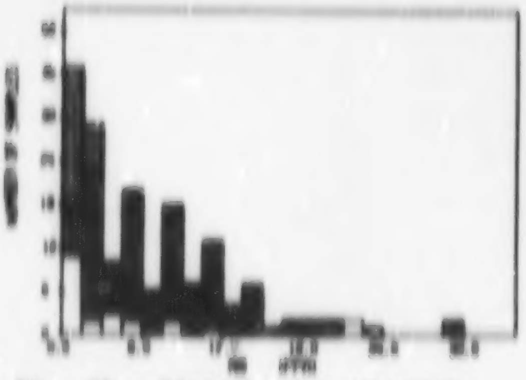

Fig. 27 - Distribution of molybdenum in coals analysed.

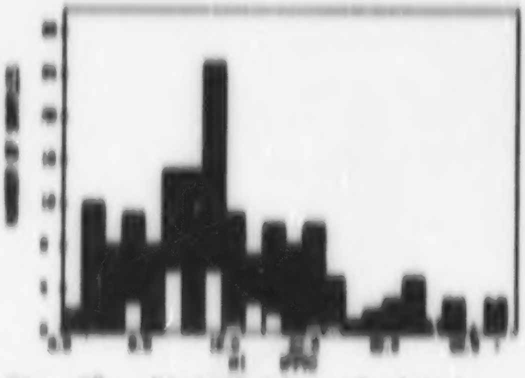

Fig. 28 - Distribution of nickel in coals analysed.

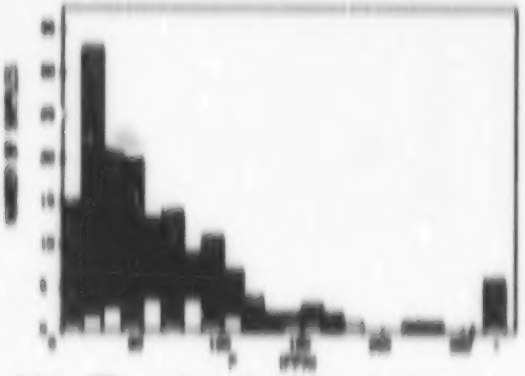

Fig. 29 - Distribution of phosphorus in coals analysed.

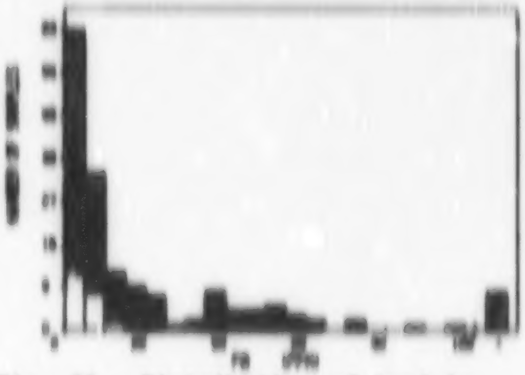

Fig. 30 - Distribution of lead in coals analysed.

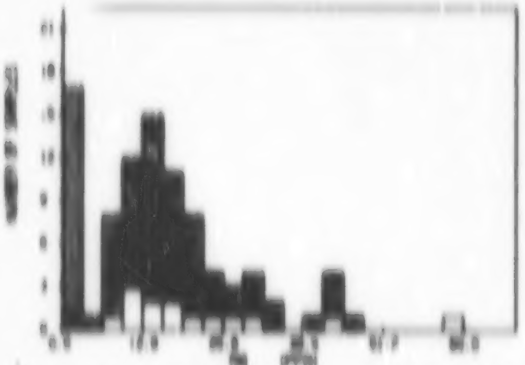

Fig. 31 - Distribution of rubidium in coals analysed.

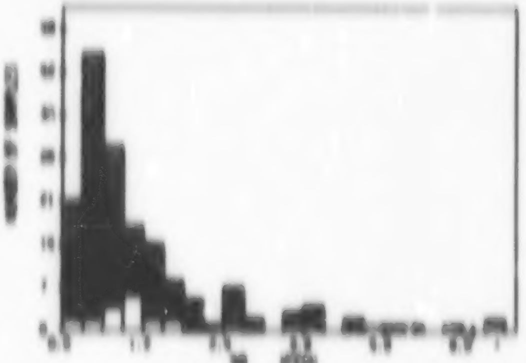

Fig. 32 - Distribution of antimony in coals analysed.

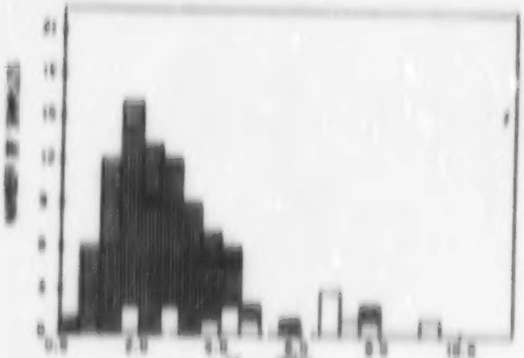

Fig. 33 - Distribution of scandium in coals analyzed.

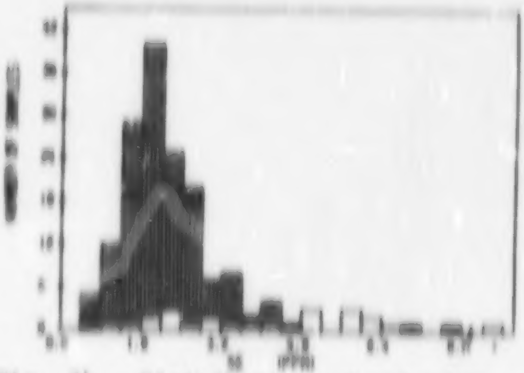

Fig. 34 - Distribution of selenium in coals analyzed.

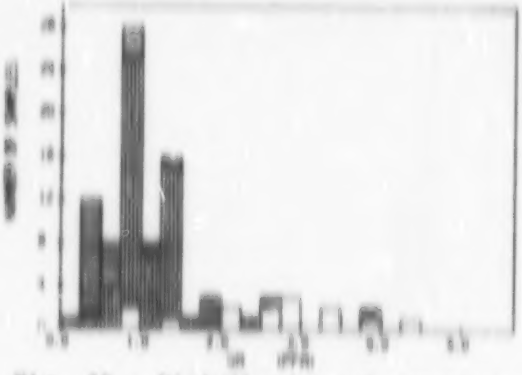

Fig. 35 - Distribution of samarium in coals analyzed.

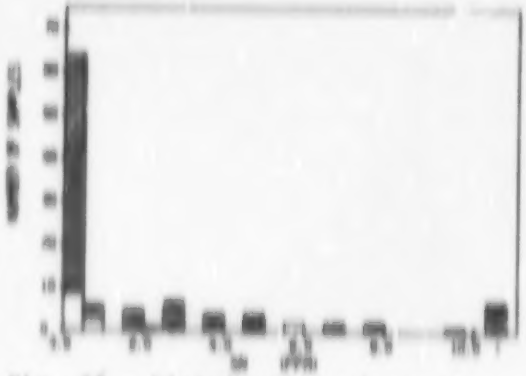

Fig. 36 - Distribution of tin in coals analyzed.

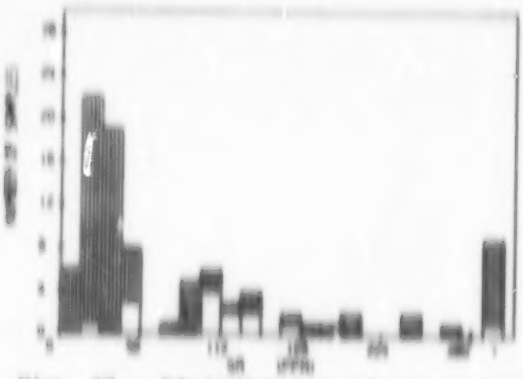

Fig. 37 - Distribution of strontium in coals analyzed.

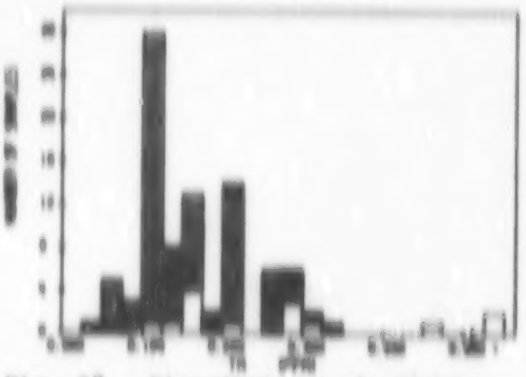

Fig. 38 - Distribution of tantalum in coals analyzed.

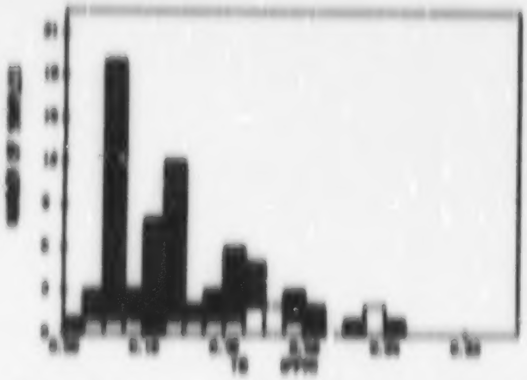

Fig. 39 - Distribution of terbium in coals analyzed.

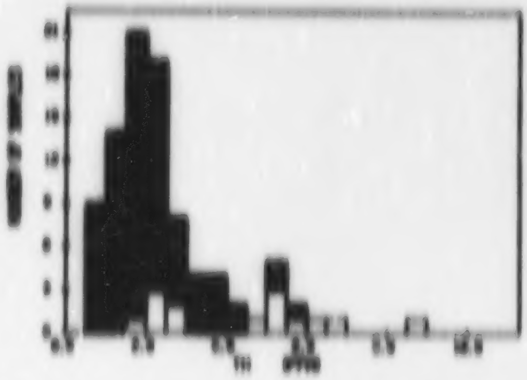

Fig. 40 - Distribution of thorium in coals analyzed.

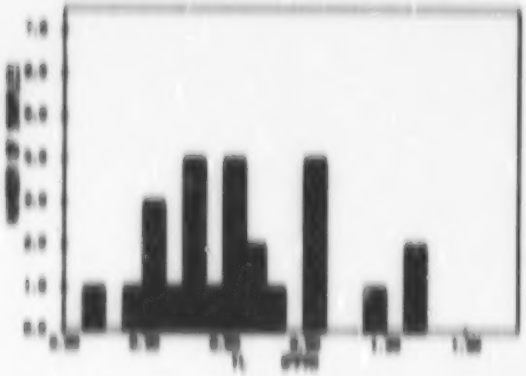

Fig. 41 - Distribution of thallium in coals analyzed.

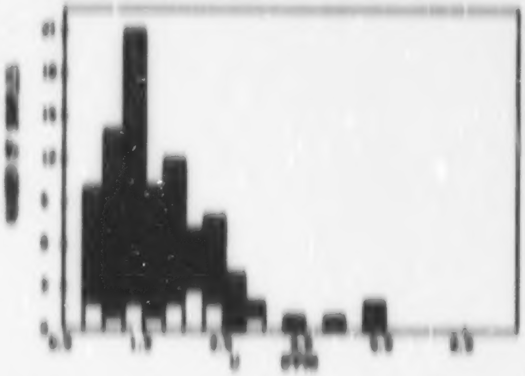

Fig. 42 - Distribution of uranium in coals analyzed.

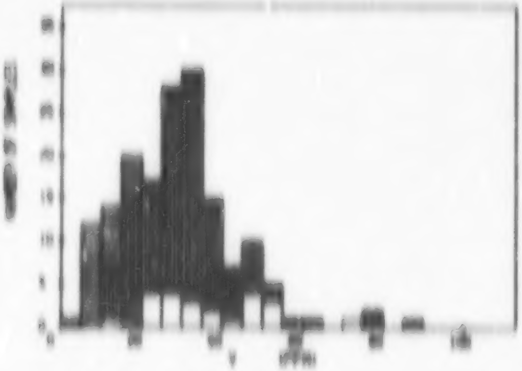

Fig. 43 - Distribution of vanadium in coals analyzed.

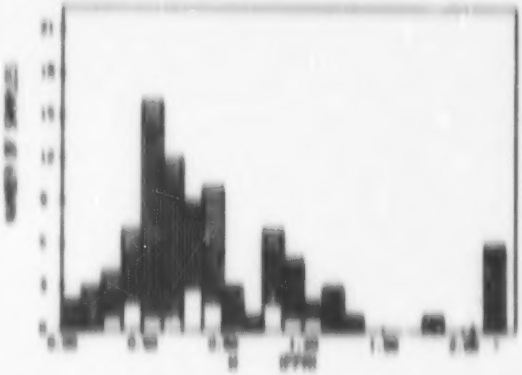

Fig. 44 - Distribution of tungsten in coals analyzed.

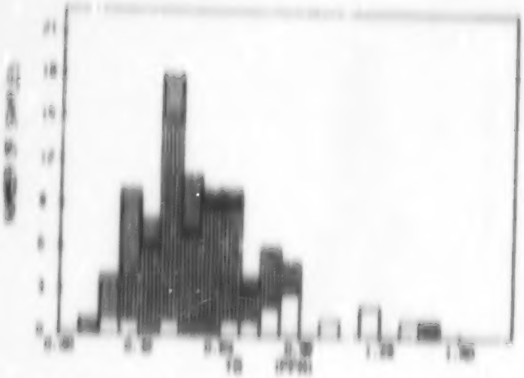

Fig. 45 - Distribution of ytterbium in coals analysed.

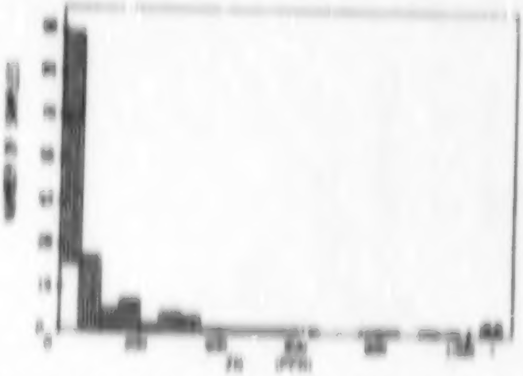

Fig. 46 - Distribution of zinc in coals analysed.

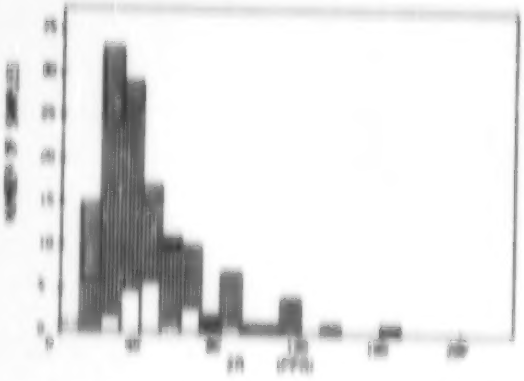

Fig. 47 - Distribution of zirconium in coals analysed.

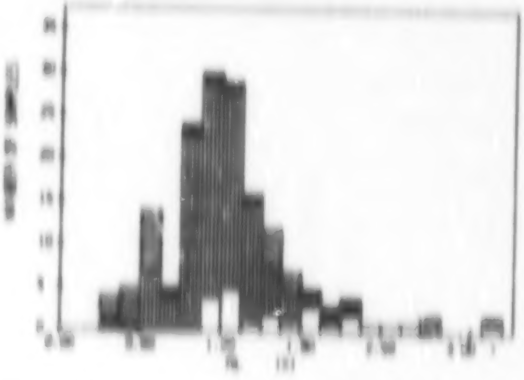

Fig. 48 - Distribution of aluminum in coals analysed.

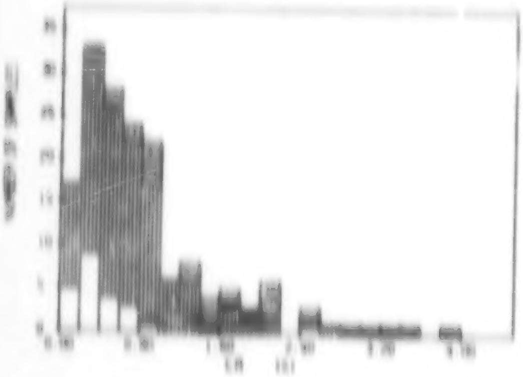

Fig. 49 - Distribution of calcium in coals analysed.

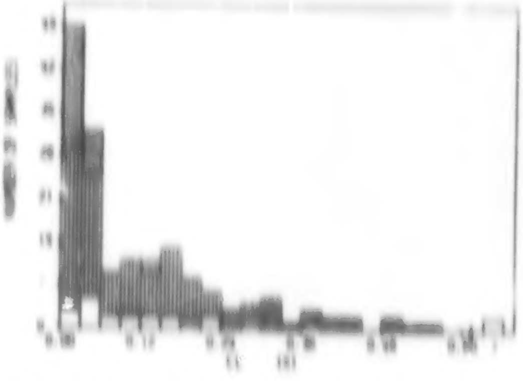

Fig. 50 - Distribution of chlorine in coals analysed.

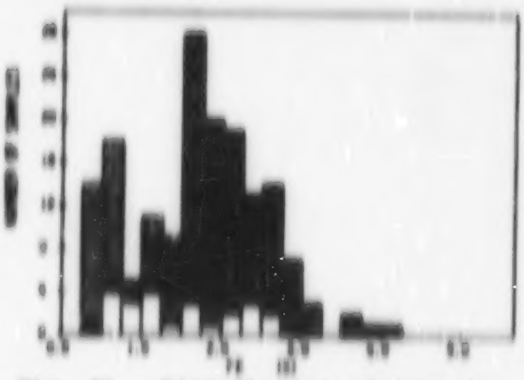

Fig. 51 - Distribution of iron in coals analysed.

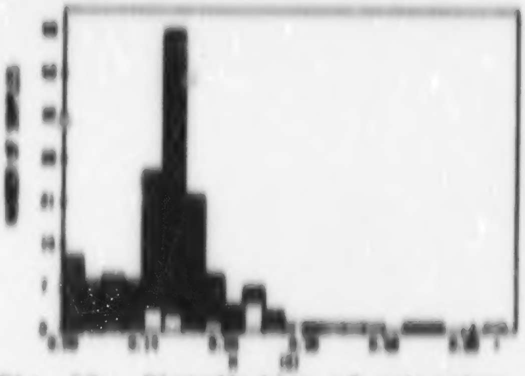

Fig. 52 - Distribution of potassium in coals analysed.

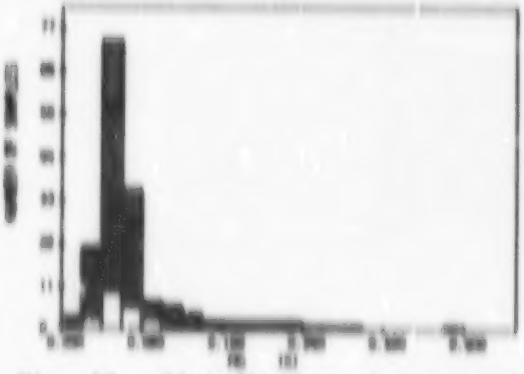

Fig. 53 - Distribution of magnesium in coals analysed.

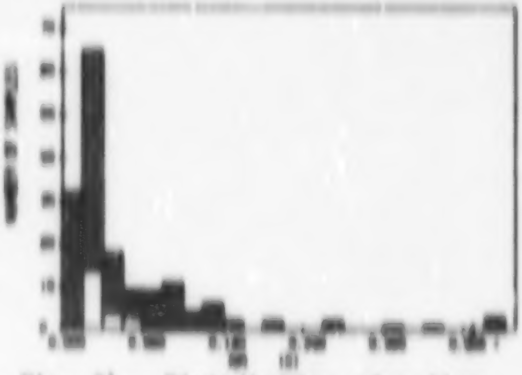

Fig. 54 - Distribution of sodium in coals analysed.

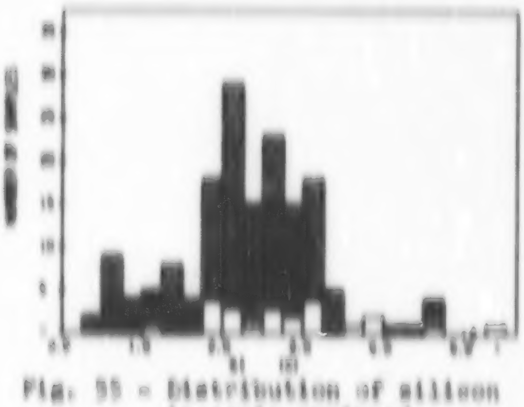

Fig. 55 - Distribution of silicon in coals analysed.

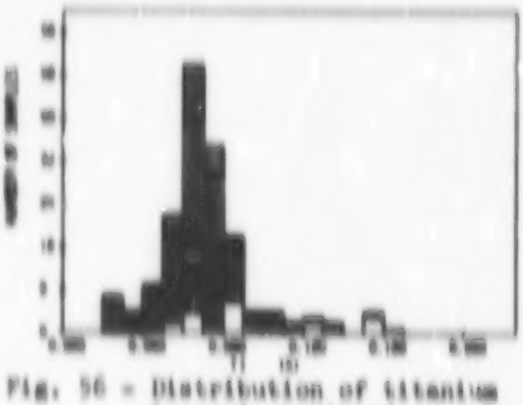

Fig. 56 - Distribution of titanium in coals analysed.

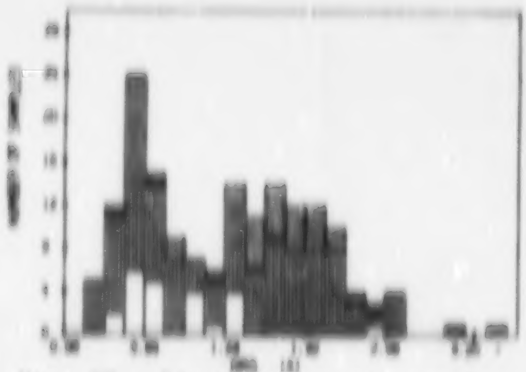

Fig. 57 – Distribution of organic sulfur in coals analyzed.

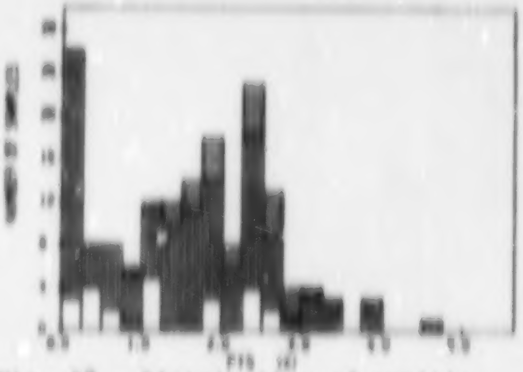

Fig. 58 – Distribution of pyritic sulfur in coals analyzed.

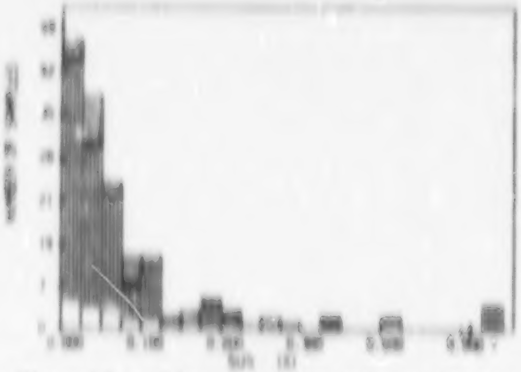

Fig. 59 – Distribution of sulfate sulfur in coals analyzed.

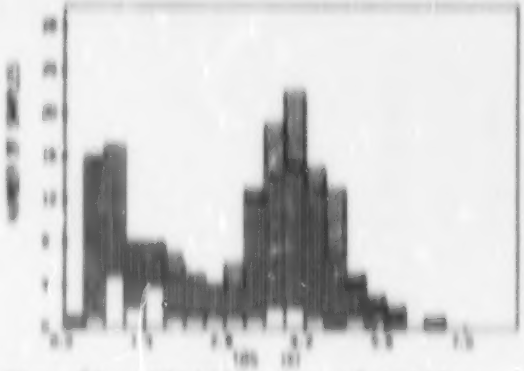

Fig. 60 – Distribution of total sulfur in coals analyzed.

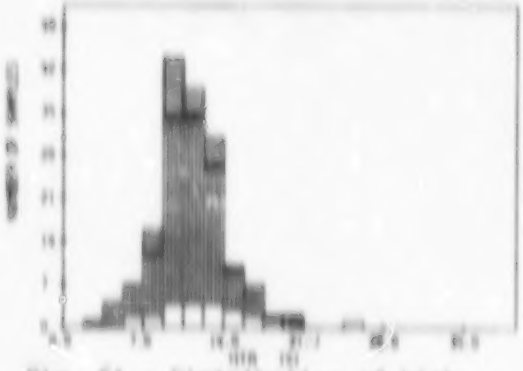

Fig. 61 – Distribution of high-temperature ash in coals analyzed.

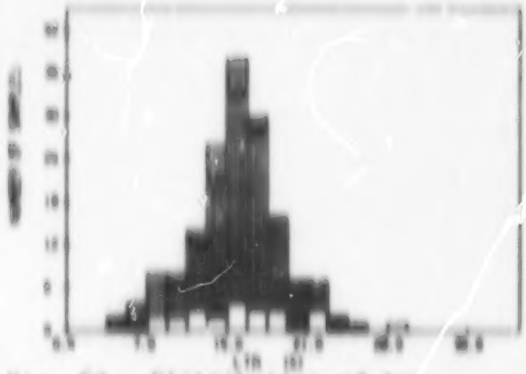

Fig. 62 – Distribution of low-temperature ash in coals analyzed.

ENRICHMENT OF ELEMENTS IN COAL

The average concentration of an element in the earth's crust is termed the "clarke." Clarke and Washington, 1924, were among the first of the geochemists to attempt to make calculations of this type. Although there are a number of difficulties in accurately estimating the clarke of an element, it is worthwhile to compare the concentrations of elements in coal with the clarke. This comparison gives an indication of the efficacy of the sum total of the coal-forming processes in "fixing" various elements in coals. The clarke values used in this report are taken from those published by Taylor, 1964, and by Turekian and Wedepohl, 1964.

Enrichment values were calculated by comparing the geometric means for the various elements with the clarkes for those elements. Enrichment values were determined for coals of the three major coal-producing areas defined previously. Ruch et al., (1974) listed only those elements that were enriched or depleted by at least an order of magnitude relative to the arithmetic mean of the concentration of an element in coals they analysed. Only a very few elements are found to be concentrated in coals; thus the use of geometric means reduces the influence of a few very high values on the data. Table 12 lists all those elements in coals that are found to be enriched by a factor of six or more. A factor of six was chosen as a matter of convenience and no special significance should be attributed to it.

Only four elements are listed on table 12, no more than three for any one of the three major areas sampled. Apparently, on the average, very few elements are found to be concentrated in coals relative to the clarke values. Boron, chlorine, and selenium are enriched in coals from the Illinois Basin; arsenic, chlorine, and selenium, in coals of eastern United States; and selenium, in coals of western United States. Individual samples may be enriched in elements other than the four listed above. Such enrichments probably indicate local mineralization and are not representative of the coals in general.

Boron is concentrated in the coals of the Illinois Basin, but not in the coals of eastern and western United States. A number of workers have used the B concentration in sediments and sedimentary rocks as an indicator of paleosalinity of the environment in which the sediment was originally deposited (Couch, 1971). Greatly oversimplified, when the technique is used, it is assumed that the relative concentrations of B in sediments and sedimentary rocks are directly dependent on the salinity of the water in which the sediments were deposited; therefore, marine sediments contain more B than nonmarine sediments. However, the interpretation of B paleosalinity from even a carefully controlled set of samples is difficult. The set of samples reported upon here was not specifically collected and was not specially treated for boron analyses. The most obvious interpretation to be made from the observation that B is concentrated in the coals of the Illinois Basin and not in the coals from eastern and western United States is that the Illinois Basin coals were deposited in waters that had a higher salinity (more brackish or more marine) than did the waters in which the other coals were deposited. In general, this interpretation agrees with other interpretations based on other criteria of the environments of deposition of the various coals. The coals of the Illinois Basin are generally more closely associated with marine strata than are the coals in the Appalachians (eastern) or in the Rocky Mountain (western) areas (Wanless et al., 1969; and Weimer, 1970).

Chlorine is concentrated in coals from the Illinois Basin and from eastern United States, but not in coals from western United States. Distribution of chlorine in coals of the Illinois Basin has been investigated by Gluskoter and Rees, 1964; Gluskoter, 1967; and Gluskoter and Ruch, 1971. In general, the chlorine content of coals in the Illinois Basin increases with depth of the coal. Coals currently being mined by surface methods are low in chlorine (less than 0.04 percent) and coals mined at the greatest depths contain the highest chlorine (0.4 to 0.6 percent). Therefore, the mean concentrations may be influenced by the distribution of samples. This may be the case with the samples from eastern United States, where many of the coals were sampled in deep mines. The population of samples is larger for the Illinois Basin; however, if any bias is present in the sampling, it would probably be a bias towards lower chlorine values.

The observed correlation of chlorine and depth to the coal bed is not a primary correlation, but it is the result of an increase in salinity of ground water with greater depth (Gluskoter, 1965a). Gluskoter and Ruch, 1971, concluded that the presence of halite (NaCl) in coal accounted for only a portion of the total chlorine present in coals from the Illinois Basin and that weakly bound chlorine in organic combination was a likely mode of occurrence.

Selenium is the third element found to be enriched in coals of the Illinois Basin. It is also enriched in coals of the eastern United States and is the only element that is enriched (at least six times the clarke) in coals sampled in western United States. Selenium is the most strongly enriched of all the elements, with enrichment factors of 26, 40, and 68, in western, Illinois Basin, and eastern coals, respectively. Selenium content of nine laboratory-prepared (washed) coals is discussed later in this report. Those data are interpreted to show selenium in both organic and inorganic combination in coals. We would suggest that at least a portion of the selenium in the coal may be inherited directly from the Se concentrated by plants in the original coal swamp. A few analyses of peats from the Okefenokee swamp in Georgia (Arthur Cohen, personal communication) do show Se concentrations of the same magnitude as those reported for the coals in Table 12.

Arsenic is found to be enriched in the samples of coals from the eastern United States. In general, arsenic is associated with the sulfide-rich fraction of the coal and most likely is in solid solution in the ferrous disulfides in coal: pyrite and marcasite. The samples of coal from eastern United States that were washed in the laboratory prior to analyses do suggest this mode of occurrence for arsenic.

In coals from all three areas most of the elemental concentrations are lower than the clarke of the elements. A value of six times the clarke was used in classifying those elements enriched in coals. If a value of one-sixth the clarke is used to define those elements depleted in coals the following are depleted in coals of the Illinois Basin: Al, Ca, Cr, F, Hf, K, Lu, Mg, Mn, Na, P, Sc, Si, Sr, Ta, and Ti. All of the other elements determined are within the range of one-sixth to six times the clarke. In general, elemental concentrations are generally lower in coals from western United States; therefore more elements are depleted relative to the clarke. In addition to most of those elements listed for coals from the Illinois Basin other elements depleted in western coals are, Be, Ce, Co, Cs, Eu, Fe, Ga, La, Ni, Rb, Sm, V, Yb, and Zn.

TABLE 12—ELEMENTS ENRICHED IN COALS

	Element	Enrichment Factor	Mean Value In Coal	Clarke
Illinois Basin (114 samples)				
	B	9.5	95 ppm	10 ppm
	Cl	6.0	800 ppm	130 ppm
	Se	40	2.0 ppm	.05 ppm
Eastern United States (23 samples)				
	As	8.2	15 ppm	1.8 ppm
	Cl	7.7	1000 ppm	130 ppm
	Se	68	3.4 ppm	.05 ppm
Western United States (29 samples)				
	Se	26	1.3 ppm	.05 ppm

NOTE: Includes only those elements that have a geometric mean concentration six times the Clarke.

ANALYSES OF BENCH SAMPLES

The variation of chemical elements vertically within a coal bed has been investigated by analyses of "bench samples" of coal. This series of five sample sets has been collected by sampling the coal seam in vertical segments or "benches". Normally, the rock unit immediately overlying the coal also was sampled, as was the underclay (or other seat rock), and any rock parting more than three-eighths inch (one centimeter) thick within the seam. Each bench of coal was analysed for the full range of chemical elements, and several of the associated rock units were also extensively analysed chemically. The analytical methods used were the same as those used to analyse the whole coal samples and are described in the appendix.

Five sets of benches were sampled and analysed in this study. All of the five sets are from the Herrin (No. 6) Coal Member in Illinois. The sample sites were selected to provide a range of geological settings and geochemical characteristics of the coals. Samples were taken from areas of high-sulfur coal and from areas of low-sulfur coal, from underground mines and from strip mines, and from areas with marine roof rocks and areas with nonmarine strata immediately overlying the coal. The five sample sites are separated geographically by as much as 305 kilometers (190 miles); and no two sites are closer than 40 kilometers (25 miles). In this discussion the five sites will be identified by numbers 1 through 5.

The thickness of each bench sample is given in table 13. Coals sampled ranged from 143 cm (56 in) to 307 cm (121 in) in thickness. The negative values shown in the table are the sampled thicknesses of the roof strata. The top of the coal was taken as a datum and was given the value of zero in each case. Those instances in which roof, floor, or rock partings were collected are noted in table 13. The noncoal units that were analysed chemically have an analysis number listed in table 13.

The results of the chemical analyses of 40 bench samples are given in tables 14 through 18. All results are reported on a whole coal basis as was done for the 172 whole coal samples. Table 14 lists the results of the analyses for trace elements; table 15, the major and minor element determinations; tables 16 and 17, the standard coal parameters; and table 18, the results of analyses for total and varieties of sulfur.

(Text continued on page 83)

TABLE 13—IDENTIFICATION OF BENCH SAMPLES ANALYZED

ANALYSIS NUMBER	STATE	ORIGIN	SAMPLE THICKNESS (CM)	REMARKS
		-- BENCH SET 1 --		
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
		-- BENCH SET 2 --		
[illegible]	[illegible]	[illegible]	[illegible]	LIMESTONE ROOF - SAMPLED, NOT ANALYZED
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	SHALE PARTING (BLUE BAND)
[illegible]	[illegible]	[illegible]	[illegible]	UNDERCLAY - SAMPLED, NOT ANALYZED
		-- BENCH SET 3 --		
[illegible]	[illegible]	[illegible]	[illegible]	SHALE ROOF - SAMPLED, NOT ANALYZED
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	SHALE PARTING - SAMPLED, NOT ANALYZED
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	UNDERCLAY - SAMPLED, NOT ANALYZED
		-- BENCH SET 4 --		
[illegible]	[illegible]	[illegible]	[illegible]	SHALE ROOF
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
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[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	SHALE PARTING (BLUE BAND)
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	UNDERCLAY
		-- BENCH SET 5 --		
[illegible]	[illegible]	[illegible]	[illegible]	SHALE ROOF
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	SHALE PARTING - NOT SAMPLED
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	UNDERCLAY

NOTE: Samples are listed by analysis numbers on tables 14 through 18.

TABLE 14—ELEMENTS IN BENCH SAMPLES
(parts per million, moisture-free whole coal basis)

SAMPLE	AG	AS	B	BA	BE	BR	CD	CE	CO	CR	CS	CU
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 14—Continued

SAMPLE	DY	EU	F	GA	GE	HF	HG	I	IN	LA	LU	MN
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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NOTE: Samples listed by sample number (D-number). Refer to table 13 for identification of samples.

TABLE 14—Continued

SAMPLE	[illegible]	[illegible]	P	PB	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	TA

TABLE 14--Concluded

SAMPLE	TB	TH	TL	U	V	W	YB	ZN	ZR
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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TABLE 15—MAJOR AND MINOR ELEMENTS IN BENCH SAMPLES
(percent, moisture-free whole coal basis)

SAMPLE	AL	CA	CL	FE	K	MG	NA	SI	TI
C18552	0.72	1.20	0.06	0.80	0.16	1.05	0.020	1.60	0.04
C18553	0.89	0.87	0.05	1.50	0.14	0.05	0.020	2.00	0.04
C18554	0.94	0.63	0.05	1.30	0.06	0.03	0.010	1.70	0.04
C18555	1.80	0.61	0.06	0.80	0.22	0.36	0.030	3.50	0.09
C18556	1.70	1.60	0.03	1.20	0.25	0.07	0.030	3.80	0.07
C18557	1.60	0.87	0.04	3.30	0.15	0.06	0.030	3.30	0.06
C18558	0.69	0.32	0.04	3.00	0.12	0.04	0.020	3.50	0.04
C18559	1.50	0.51	0.04	2.50	0.27	0.06	0.050	3.80	0.06
C18704	1.70	1.00	0.18	1.60	0.33	0.16	0.160	5.30	0.07
C18705	0.61	1.10	0.18	1.80	0.10	0.04	0.100	1.30	0.03
C18706	0.72	1.00	0.15	2.20	0.07	0.09	0.100	1.60	0.03
C18707	1.00	0.57	0.15	1.50	0.18	0.07	0.150	3.80	0.10
C18708	1.30	0.64	0.17	1.20	0.15	0.06	0.160	2.63	0.07
C18709	1.60	0.59	0.12	1.30	0.20	0.09	0.160	3.90	0.08
C18710	4.30	0.07	0.03	5.80	0.81	0.17	0.160	7.60	0.09
C18711	1.20	1.00	0.12	2.90	0.14	0.06	0.140	2.50	0.05
C18728	0.36	0.32	0.52	0.20	0.05	0.03	0.100	0.66	0.03
C18729	0.54	1.16	0.58	0.80	0.07	0.06	0.120	0.93	0.03
C18730	0.69	0.17	0.49	0.30	0.08	0.06	0.130	1.30	0.05
C18731	0.99	0.94	0.50	0.20	0.12	0.05	0.120	1.80	0.07
C18732	1.90	0.62	0.47	0.50	0.25	0.09	0.140	3.80	0.07
C18733	1.10	0.59	0.49	0.60	0.13	0.09	0.120	2.30	0.06
C18806	6.80	0.10	0.01	1.30	0.20	0.43	0.610	15.00	0.14
C18807	0.52	0.38	0.06	1.80	0.17	0.06	0.020	1.50	0.03
C18808	0.29	0.30	0.06	6.80	0.01	0.05	0.030	0.51	0.01
C18809	0.83	0.51	0.04	0.50	0.10	0.05	0.050	1.70	0.08
C18810	4.50	0.17	0.03	0.80	0.52	0.16	0.140	7.90	0.16
C18811	1.20	0.95	0.02	1.80	0.13	0.05	0.090	2.10	0.03
C18812	1.80	0.26	0.03	1.00	0.28	0.10	0.060	3.90	0.09
C18813	11.00	0.10	0.01	0.90	0.85	0.22	0.360	17.00	0.24
C18814	0.81	1.00	0.01	3.30	0.10	0.06	0.080	1.90	0.04
C18815	5.00	0.26	0.06	1.10	1.20	0.51	0.600	16.00	0.19
C18982	5.30	0.30	0.01	1.30	0.50	0.70	0.590	13.00	0.12
C18983	0.73	0.68	0.10	0.90	0.18	0.09	0.030	1.50	0.05
C18984	0.93	0.80	0.12	1.10	0.15	0.05	0.040	1.70	0.05
C18985	1.00	0.33	0.13	1.20	0.13	0.05	0.040	1.80	0.06
C18986	0.55	0.11	0.13	1.20	0.03	0.03	0.030	0.75	0.02
C18987	1.50	0.35	0.11	1.50	0.11	0.05	0.090	2.20	0.08
C18988	2.30	0.29	0.09	1.80	0.55	0.15	0.070	4.20	0.10
C18989	8.80	0.21	0.09	1.80	3.80	0.88	0.520	18.00	0.20

NOTE: Samples listed by sample number (C-number). Refer to table 1 for identification of samples.

TABLE 16—PROXIMATE ANALYSES OF BENCH SAMPLES
[percent of whole coal except for Btu values]

TABLE 17—ULTIMATE ANALYSES OF BENCH SAMPLES
[percent, moisture-free whole coal basis]

NOTE: Abbreviations are listed in table 1 and identification of samples are in table 15. All values are on a moisture-free whole coal basis except for air-dry loss (ADL) and moisture (MOIS).

TABLE 18—SULFUR ANALYSES OF BENCH SAMPLES
(percent, moisture-free, whole coal basis)

SAMPLE	ORS	PYS	SUS	TOS	SERF
C18552	2.30	0.37		2.67	2.60
C18553	2.41	1.92	0.01	4.34	4.30
C18554	2.49	1.48	0.01	3.98	4.32
C18555	2.45	0.94	0.01	3.40	3.21
C18556	2.35	1.86		4.22	3.61
C18557	1.45	6.63	0.03	8.11	8.27
C18558	1.77	5.15	0.01	6.93	6.97
C18559	1.94	4.52	0.01	6.47	6.47
C18704	3.08	1.32	0.23	4.63	4.65
C18705	2.71	1.74	0.13	4.61	4.81
C18706	2.63	2.51	0.15	5.29	4.88
C18707	2.22	1.70	0.15	4.07	3.87
C18708	2.70	1.24	0.11	4.05	3.78
C18709	2.68	2.15	0.20	5.03	3.88
C18710	2.14	21.99	0.81	24.94	
C18711	2.05	3.45	0.65	6.95	0.63
C18728	1.13	0.02	0.01	1.17	1.08
C18729	0.55	0.28	0.02	0.85	0.94
C18730	0.52	0.18	0.01	0.70	0.86
C18731	0.60	0.03	0.02	0.65	0.74
C18732	0.42	0.02	0.02	0.46	0.60
C18733	0.40	0.31	0.05	0.76	0.99
C18806	0.24	1.86	0.12	2.22	1.77
C18807	1.87	1.75	0.03	3.65	3.85
C18808	0.58	15.18	0.23	15.99	
C18809	1.91	0.33	0.01	2.24	2.47
C18810	1.35	1.10	0.02	2.47	2.50
C18811	2.10	2.32	0.04	4.46	4.24
C18812	1.85	0.91	0.03	2.79	2.90
C18813	0.19	1.33	0.20	1.73	1.84
C18814	0.92	5.91	0.13	6.95	6.84
C18815	0.02	0.80	0.08	0.90	0.85
C18982	0.26	2.41	0.09	2.75	2.85
C18983	1.86	0.84	0.02	2.75	3.03
C18984	1.89	1.05	0.05	3.00	3.12
C18985	1.70	1.25	0.02	2.97	3.05
C18986	1.88	1.16	0.04	3.08	3.47
C18987	1.68	1.41	0.06	3.15	3.15
C18988	1.48	2.12	0.05	3.65	3.68
C18989	0.0	0.92	0.05	0.98	0.42

NOTE: Refer to table 1 for abbreviations; refer to table 11 for identification of samples.

Because coal in most respects is a heterogenous material, wide variations in content of trace elements in individual benches were expected, and in general that was the finding. However, in several bench sets some elements occur uniformly throughout the bed. Among the more uniform distributions observed is that of bromine in bench set 3 (fig. 63). The rare earth elements also exhibit relatively uniform distributions in the bench sets analysed. Figure 63 and all of the histograms of bench samples represent the total coal seam and are drawn with the proportional thickness of each bench plotted along the ordinate and the concentration of the elements plotted along the abscissa. The top of the coal seam, or the rock above the seam, is plotted at the top of each figure.

The expected variability in trace element distribution is apparent in figure 64. The three elements U, Mo, and V have a wide distribution range and all are concentrated in the uppermost bench of this sample set. Although maximum concentration of elements may occur in any of the benches of the coal bed, the top and/or bottom benches appear to be the preferred sites. The concentration of antimony in the uppermost bench of four samples sets and in the bottommost bench of the fifth is represented in figure 65. The maximum concentration within the coal bed is in either the top or bottom bench of each sample set. Still higher amounts of antimony were obtained from the rock units associated with the coals.

Distribution of germanium in the bench sets is shown in figure 66. The pattern is distinct and consistent in bench sets 1 through 4, and less well defined in bench set 5. The germanium content of the top bench and/or that of the bottom bench are greater than the germanium content of the other benches in all five sample sets. Earlier efforts, (Ruch et al., 1974, and Gluskoter, 1975) and those of Zubovic (1966), demonstrated that germanium is primarily associated with the organic fraction of the coals in Illinois and not in the mineral matter fraction. This and the observation that the germanium is concentrated at the boundaries of the coal bed, the top and the bottom, suggest that the germanium was introduced into the coal bed after burial and thus its origin is not related to conditions in the swamps in which the coal was formed. Rather, the germanium was transported into the coal bed in solution and was assimilated by the coal when geochemical conditions within the coal bed were favorable for the removal of the germanium from the solutions. The horizontal boundaries (top and bottom) of the bed were necessarily in contact with those solutions before the innermost parts of the bed. Zubovic et al., (1964) presents a different interpretation for the concentration of elements at the top and the bottom of the coal beds in the Illinois Basin. He attributes these concentrations to "greater availability of mineral matter and mineral- rich solutions toward the beginning and end of the interval of accumulation of the plant debris that eventually becomes coal." (Zubovic et al., 1964, p. 635). He also stated the belief that coals near the margin of the basin of deposition would have a more heterogenous vertical distribution of elements because of variable conditions of weathering and erosion in the border land.

Bench sets 1, 2, 3, and 4 are from locations in south central and southwestern Illinois and bench set 5 is from the northwestern part of the coal basin and is interpreted to have been closer to the basin margin. The germanium distribution is somewhat more uniform in bench set 5 than in the other four bench sets; the Ge content is of the same order of magnitude as that of the other bench sets.

Elements that were observed to be closely related in face channel samples of coals are, as expected, also closely correlated in the individual benches. Examples of this are shown by calcium and manganese in bench set 1, phosphorus and fluorine in bench set 2, and sulfur and arsenic in bench set 4 (fig. 67). Calcium and Mn are associated in the mineral calcite, P and F in the mineral apatite, and S and As in the mineral pyrite. Elements that occur in coals as discrete mineral phases have wide ranges in concentrations in benches as they do in whole coal samples. For example, Zn, which occurs as the mineral sphalerite (ZnS), ranges from 17 ppm to 4100 ppm in benches of set 2. The ratio of the highest concentration of an element in the benches to the lowest concentration of that element in the benches is a measure of the range of an element within a bench set. This ratio commonly has the value of 3 to 7 or 8. The ratio is much higher for zinc in bench set 2 where it is more than 200. The other elements that are generally found concentrated in individual benches and often at the top and/or the bottom of the bed also have high ratios. Germanium in bench sets 1 through 4 has values of 24 to 260; Mo in all five sets has a range ratio of 18 to 480; and Cl in bench sets 1 and 4 has values of 70 and 60 for this ratio.

In general, elements that have low values of the ratio showing range in concentration of an element in a single bench set include boron and bromine. Values of the ratio of 1.5 and less for these elements are found in several but not in all the bench sets. Bench set 4 has a value of 1 for B and bench set 1 has a value of 5 for Br.

The roof shale, underclay, and a clay parting (blue band) were analysed, as well as the seven benches of coal in bench set 4. Roof and floor were also analysed in bench set 5, and a clay parting (blue band) was analysed in bench set 2. Many elements including Al, Ba, Cd, Co, Cr, Cs, Cu, F, Ga, Hf, La, Mn, Sc, Se, Sm, Sr, Th, V, Yb, Zr, K, Mg, Si, Na, and most of the rare earth elements that were determined, occur in significantly higher concentrations in most of these rock units than in the coals. Examples of concentrations of the elements in the strata associated with the coal are given in the illustrations of concentrations of barium, cerium, and silicon in bench set 5 (fig. 68).

(Text continued on page 88)

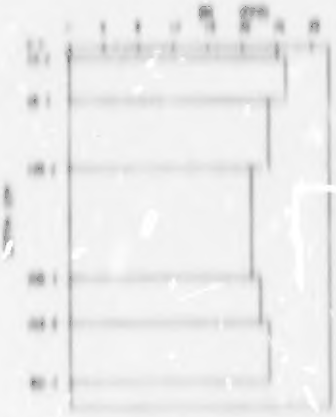

Fig. 63 - Distribution of bromine in coals of bench set 1.

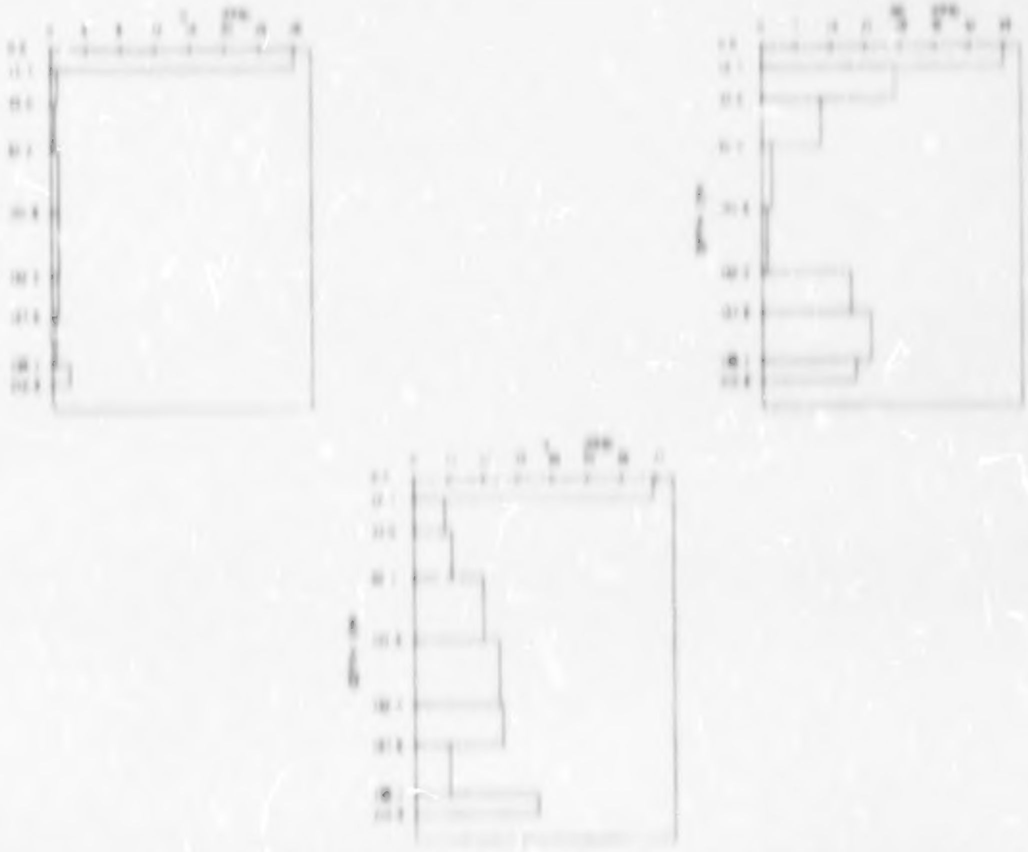

Fig. 64 - Distribution of uranium, molybdenum, and vanadium in coals of bench set 1.

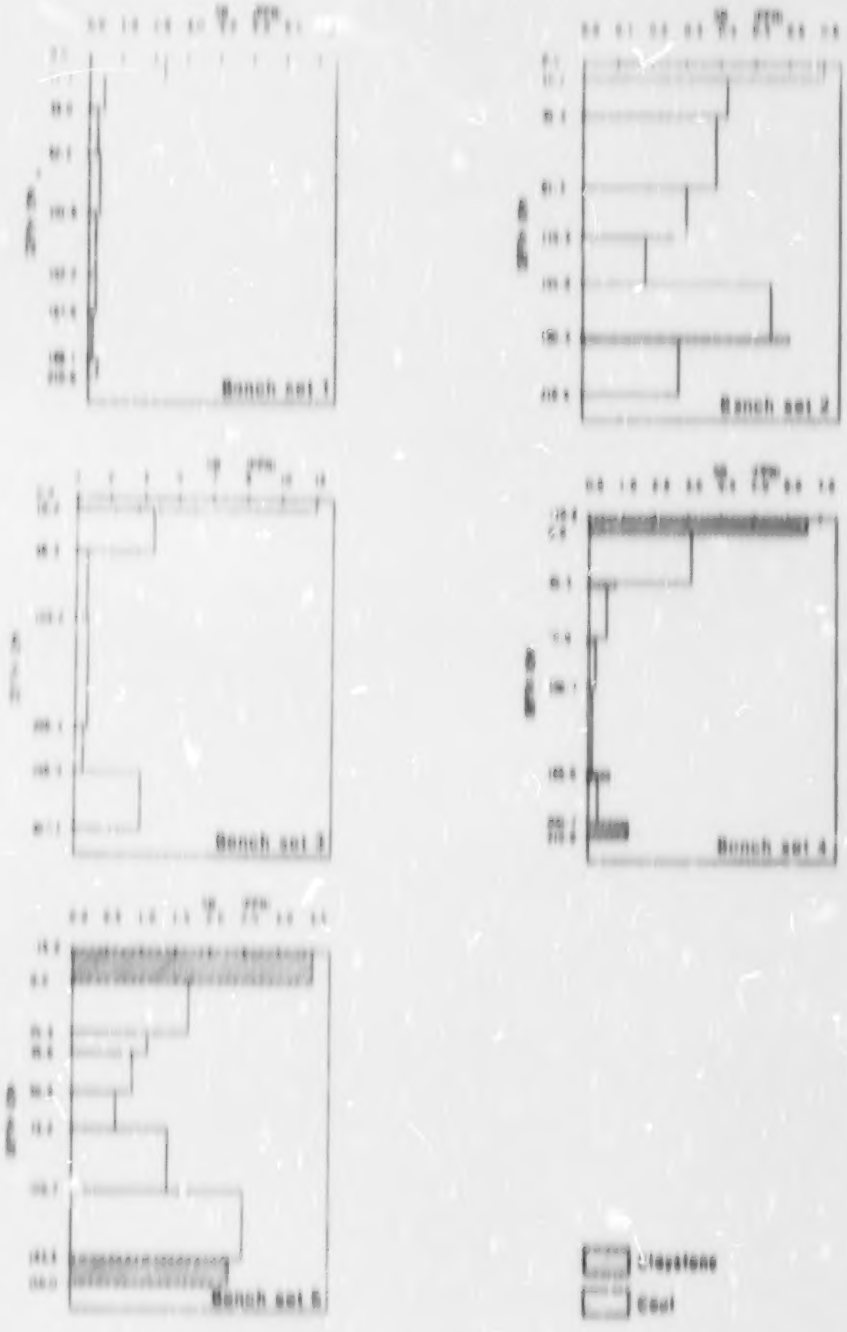

Fig. 65 - Distribution of antimony in coals from bench sets 1, 2, 3, 4, and 5.

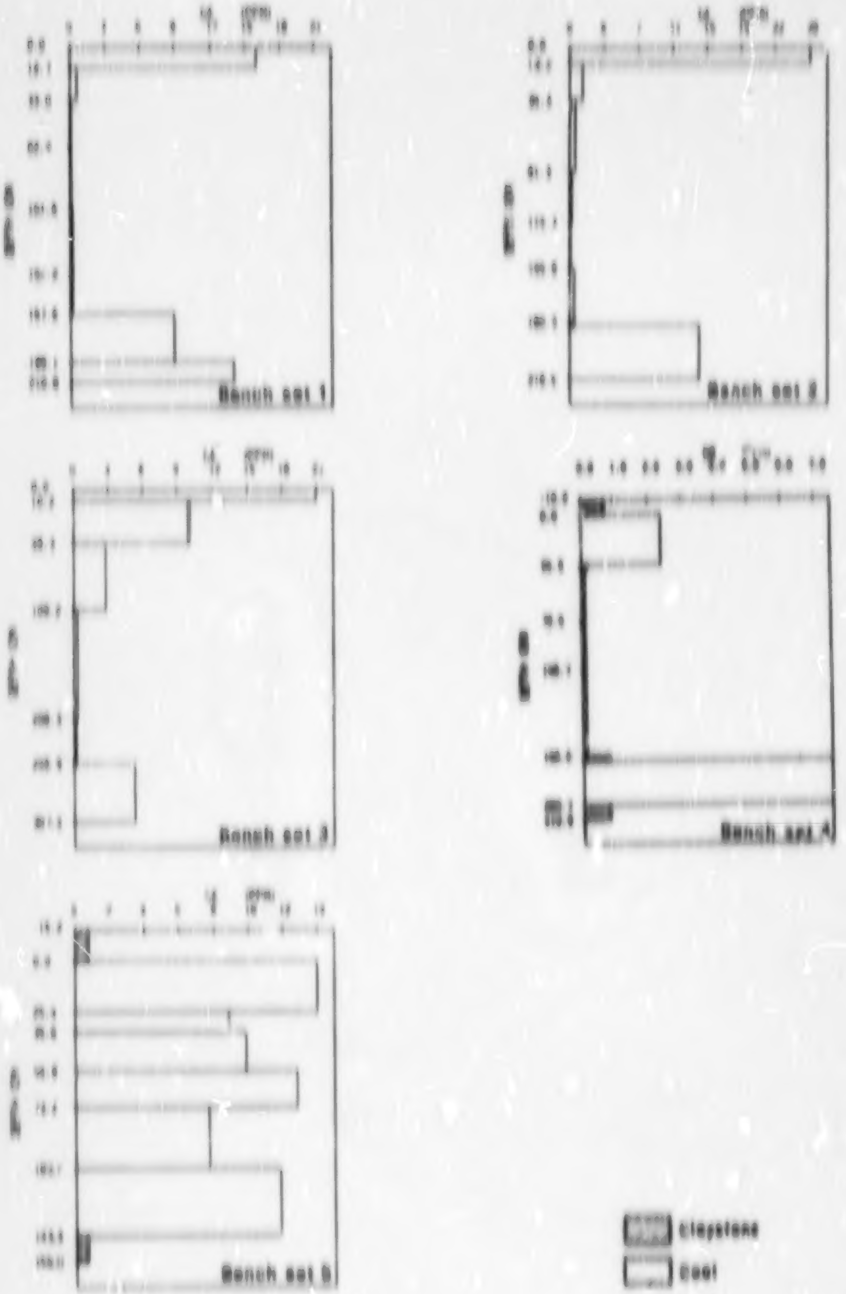

Fig. 66 - Distribution of germanium in coals from bench sets 1, 2, 3, 4, and 5.

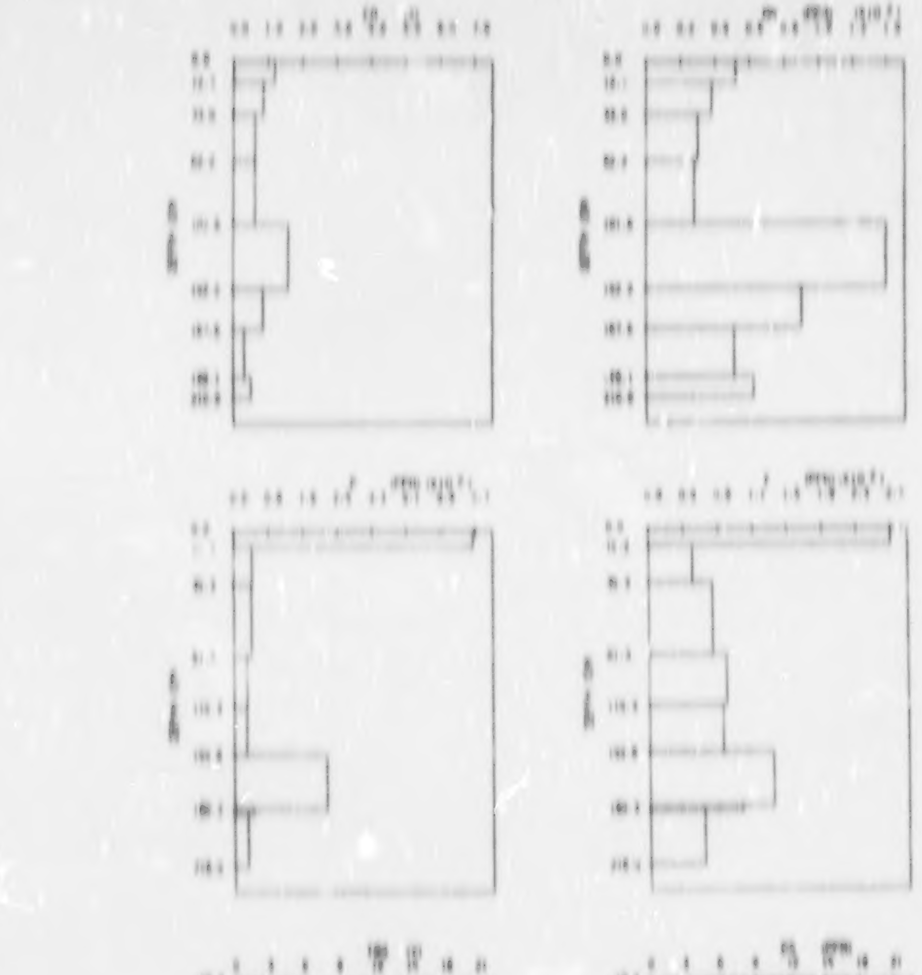

Fig. 67 - Distribution of associated elements in bench sets: Calcium and manganese in bench set 1; phosphorus and fluorine in bench set 2; and total sulfur and arsenic in bench set 4.

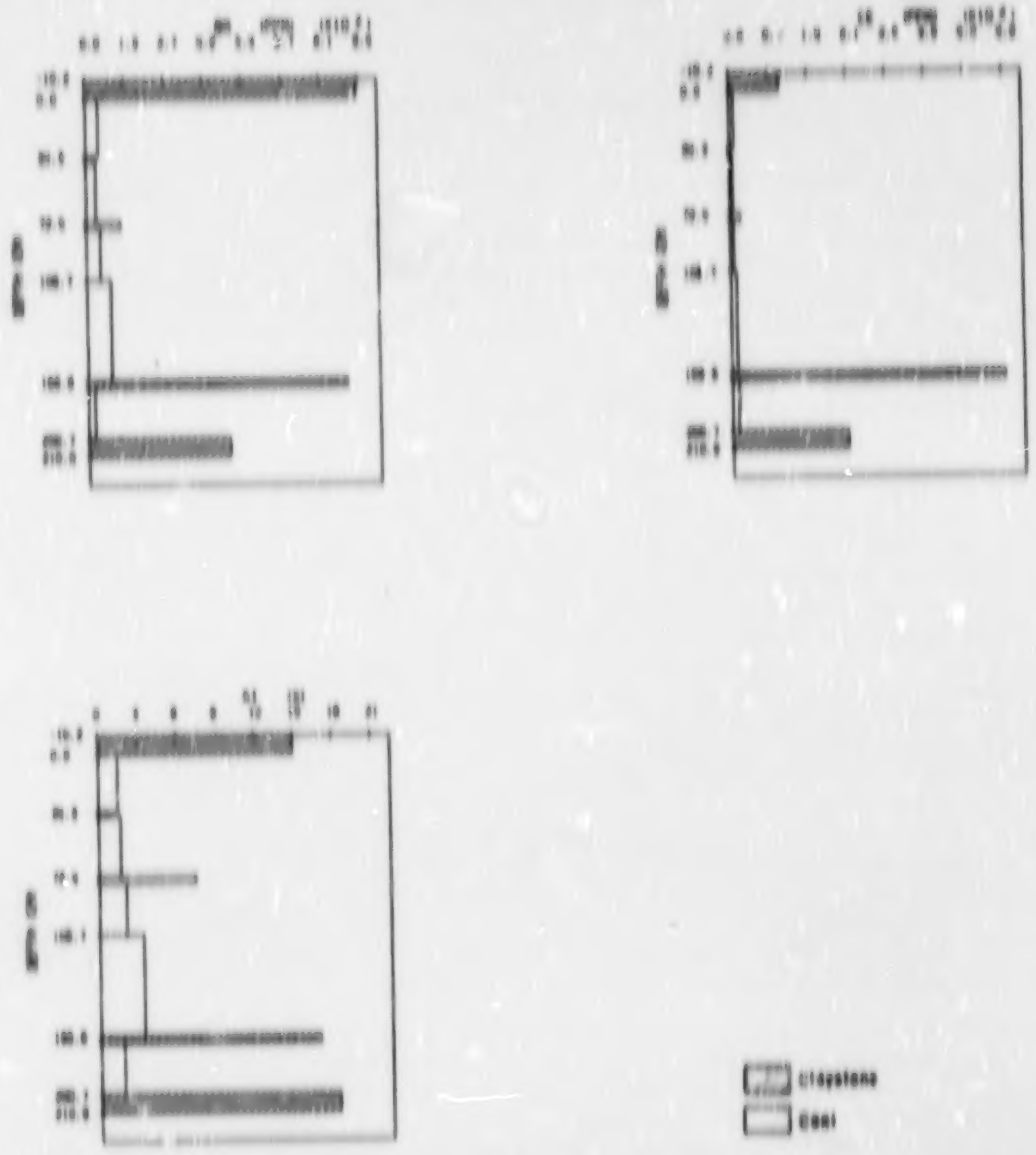

Fig. 68 - Concentration of barium, cerium, and silicon in coals and associated strata of bench set 4.

ANALYSES OF WASHED COALS

Methods of Analyses

Many of the coals mined in the United States are "washed" or "cleaned" prior to delivery to the consumer. Cleaning involves reducing the content of ash and sulfur of the coal by removing a portion of the mineral matter associated with the coal. Because the specific gravities of the minerals in coal are from two to four times greater than that of the coal, most coal-cleaning techniques involve a specific gravity separation. Data on the washability of Illinois coals and a description of the techniques used have been published by Helfinstine et al., (1970) and Helfinstine et al., (1971,1974).

Nine samples of coals were separated into specific gravity fractions and were analysed for most of the same major, minor, and trace elements as were the 172 whole coals. The gravity separations were, in each case, made on a three-eighths inch by 28 mesh size fraction obtained by crushing the coal to less than three-eighths inch (1 cm) and then screening it. All separations of 1.60 specific gravity and below were made in an appropriate mixture of perchloroethylene and naphtha. The separations at a specific gravity of approximately 2.8 were made in bromoform or in bromoform that contained a small amount of ethyl alcohol. Three coals were each separated into six specific gravity fractions in the perchloroethylene and naphtha; the heaviest of each of these six fractions (1.60 sink) was separated into two parts in bromoform. Five of the coals were washed to a maximum gravity of only 1.60. One coal was also separated in the perchloroethylene and naphtha but only two fractions were analysed, one with a specific gravity of less than 1.25 and one with a specific gravity greater than 1.60. The results of the analyses for Cl and I in the washed coals are not given, because relatively large amounts of these elements may have been added to the coals from the washing media.

Five of the coals that were washed were from the Illinois Basin, one each from the Davis Coal Member, the DeKoven Coal Member, and the Colchester (No. 2) Coal Member, and two were from the Herrin (No. 6) Coal Member. Three of the samples were from the eastern coal fields; a sample of the Blue Creek bed, Alabama; the Pocahontas No. 4 bed, West Virginia; and the Pittsburgh No. 8 bed, West Virginia. The remaining sample was from the Black Mesa Field in Arizona. The samples are identified and the percent of the raw coal in each washed fraction is given in Table 19.

Results of the determinations of trace elements of the laboratory-prepared coals are given in table 20; the major and minor elements in table 21; the standard coal analyses in tables 22 and 23; and the varieties of sulfur in table 24. Samples are listed in order of increasing specific gravity. Those samples identified as to their size distribution (for example, three-eighths inch by 28 mesh) are "whole coal," or the sample prior to washing. The analyses of the 28 mesh by zero fraction is also given, although this fraction was removed from the coal prior to washing to avoid the difficulties that are encountered when attempts are made to wash fine coal. No significantly different concentrations of elements in the 28 mesh by zero fraction are observed when compared to the three-eighths inch by 28 mesh fraction.

(Text continued on page 103)

TABLE 19--IDENTIFICATION OF LABORATORY-PREPARED WASHED COAL SAMPLES

ANALYSIS NUMBER	STATE	ORIGIN	SPECIFIC GRAVITY FRACTION	PERCENT OF RAW COAL
		-- FLOAT-SINK SET 1 --		
C-18562	ILLINOIS	HERRIN (NO.6)	28M X 0	
C-18563	ILLINOIS	HERRIN (NO.6)	1.29 F	38.1
C-18564	ILLINOIS	HERRIN (NO.6)	1.33 FS	20.9
C-18565	ILLINOIS	HERRIN (NO.6)	1.40 FS	18.6
C-18566	ILLINOIS	HERRIN (NO.6)	1.60 FS	12.5
C-18567	ILLINOIS	HERRIN (NO.6)	1.60 S	8.1
		-- FLOAT-SINK SET 2 --		
C-18889	ALABAMA	BLUE CREEK	28M X 0	
C-18878	ALABAMA	BLUE CREEK	1.30 F	25.3
C-18879	ALABAMA	BLUE CREEK	1.32 FS	20.5
C-18880	ALABAMA	BLUE CREEK	1.40 FS	36.0
C-18881	ALABAMA	BLUE CREEK	1.60 FS	11.8
C-18882	ALABAMA	BLUE CREEK	1.60 S	6.4
		-- FLOAT-SINK SET 3 --		
C-18890	W VIRGINIA	POCAHONTAS #4	3/8 X 28M	
C-18891	W VIRGINIA	POCAHONTAS #4	28M X 0	
C-18883	W VIRGINIA	POCAHONTAS #4	1.30 F	24.7
C-18884	W VIRGINIA	POCAHONTAS #4	1.33 FS	25.3
C-18885	W VIRGINIA	POCAHONTAS #4	1.40 FS	25.0
C-18886	W VIRGINIA	POCAHONTAS #4	1.59 FS	14.1
C-18887	W VIRGINIA	POCAHONTAS #4	1.59 S	10.9
		-- FLOAT-SINK SET 4 --		
C-18892	W VIRGINIA	PITTSBURGH #8	3/8 X 28M	
C-18893	W VIRGINIA	PITTSBURGH #8	28M X 0	
C-18894	W VIRGINIA	PITTSBURGH #8	1.29 F	33.8
C-18895	W VIRGINIA	PITTSBURGH #8	1.32 FS	20.9
C-18896	W VIRGINIA	PITTSBURGH #8	1.40 FS	25.7
C-18897	W VIRGINIA	PITTSBURGH #8	1.59 FS	13.5
C-18898	W VIRGINIA	PITTSBURGH #8	1.59 S	6.1
		-- FLOAT-SINK SET 5 --		
C-19014	ARIZONA	BLACK MESA FIELD	28M X 0	
C-19009	ARIZONA	BLACK MESA FIELD	1.28 F	25.0
C-19010	ARIZONA	BLACK MESA FIELD	1.30 FS	26.4
C-19011	ARIZONA	BLACK MESA FIELD	1.40 FS	40.8
C-19012	ARIZONA	BLACK MESA FIELD	1.60 FS	6.9
C-19013	ARIZONA	BLACK MESA FIELD	1.60 S	1.0

NOTE: Samples are listed by analysis numbers on tables 20 through 24.

TABLE 19--Concluded

ANALYSIS NUMBER	STATE	ORIGIN	SPECIFIC GRAVITY FRACTION	PERCENT OF RAW COAL
		-- FLOAT-SINK SET 6 --		
C-18090	ILLINOIS	DAVIS	3/8 X 28M	
C-18094	ILLINOIS	DAVIS	1.28 F	25.9
C-18095	ILLINOIS	DAVIS	1.30 FS	19.5
C-18096	ILLINOIS	DAVIS	1.32 FS	19.7
C-18097	ILLINOIS	DAVIS	1.50 FS	19.3
C-18098	ILLINOIS	DAVIS	1.60 FS	7.2
C-18099	ILLINOIS	DAVIS	1.60 S	0.5
C-18106	ILLINOIS	DAVIS	2.89 FS	3.8
C-18107	ILLINOIS	DAVIS	2.89 S	4.8
		-- FLOAT-SINK SET 7 --		
C-18092	ILLINOIS	DEKOVEN	3/8 X 28M	
C-18100	ILLINOIS	DEKOVEN	1.29 F	19.4
C-18105	ILLINOIS	DEKOVEN	1.60 S	9.0
		-- FLOAT-SINK SET 8 --		
C-18133	ILLINOIS	COLCHESTER (NO.2)	3/8 X 28M	
C-18134	ILLINOIS	COLCHESTER (NO.2)	28M X 0	
C-18135	ILLINOIS	COLCHESTER (NO.2)	1.25 F	28.2
C-18136	ILLINOIS	COLCHESTER (NO.2)	1.26 FS	23.5
C-18137	ILLINOIS	COLCHESTER (NO.2)	1.30 FS	27.5
C-18138	ILLINOIS	COLCHESTER (NO.2)	1.50 FS	10.6
C-18139	ILLINOIS	COLCHESTER (NO.2)	1.60 FS	3.2
C-18140	ILLINOIS	COLCHESTER (NO.2)	1.60 S	6.8
C-18141	ILLINOIS	COLCHESTER (NO.2)	2.89 FS	3.5
C-18142	ILLINOIS	COLCHESTER (NO.2)	2.89 S	3.2
		-- FLOAT-SINK SET 9 --		
C-18121	ILLINOIS	HERRIN (NO.6)	3/8 X 28M	
C-18122	ILLINOIS	HERRIN (NO.6)	28M X 0	
C-18123	ILLINOIS	HERRIN (NO.6)	1.25 F	36.1
C-18124	ILLINOIS	HERRIN (NO.6)	1.29 FS	17.9
C-18125	ILLINOIS	HERRIN (NO.6)	1.33 FS	14.7
C-18126	ILLINOIS	HERRIN (NO.6)	1.50 FS	9.3
C-18127	ILLINOIS	HERRIN (NO.6)	1.60 FS	6.9
C-18128	ILLINOIS	HERRIN (NO.6)	1.60 S	15.6
C-18129	ILLINOIS	HERRIN (NO.6)	2.89 FS	12.7
C-18130	ILLINOIS	HERRIN (NO.6)	2.89 S	2.9

NOTE: Samples are listed by analysis numbers on tables 20 through 24.

TABLE 20—TRACE ELEMENTS IN LABORATORY-PREPARED WASHED COAL SAMPLES
(parts per million, moisture-free, whole coal basis)

SAMPLE	AG	AS	B	BA	BE	BR	CD	CE	CO	CR	CS	CU
C18094		8.2	22		3.0		1.7		3.0	10		11
C18095		0.70	29		2.8		0.10		2.0	7.0		6.0
C18095		1.1	35		3.0		0.20		3.0	8.0		5.0
C18096		1.5	30		4.1		0.20		6.0	16		7.0
C18097		4.1	31		2.8		0.50		5.0	11		16
C18098		12	67		2.8		0.90		3.0	61		11
C18099		61	9.0		1.8		60		6.0	61		16
C18106		36	36		0.7		2.6		10	27		63
C18107		60	3.0		0.7		36		60	70		16
C18092		15	26		4.8		0.60		6.0	16		11
C18100		2.9	35		7.0		0.10		12	16		7.0
C18105		180			7.1		2.6		10	68		17
C18133		110			5.5		67		10	16		36
C18134		61	90		3.2		20		8.0	10		36
C18135		19	70		2.6		0.10		5.0	9.0		18
C18136		22	100		3.2		0.20		8.0	9.0		17
C18137		67	170		3.2		0.80		8.0	5.0		20
C18178		63	100		3.5		1.2		15	13		23
C18139		160	98		3.1		11		15	18		68
C18140		630	62		7.0		390		10	190		190
C18131		350	58		5.1		68		19	61		110
C18142		1100			5.2		110		12	62		160
C18121		15	39		2.8		6.1		3.0	32		23
C18122		11	160		2.5		1.8		5.0	25		25
C18123		0.90	90		2.3		0.20		2.0	8.0		3.0
C18124		1.5	120		1.0		0.20		3.0	12		7.0
C18125		2.1	190		1.0		0.20		6.0	16		10
C18126		5.2	68		1.0		0.50		6.0	23		11
C18127		5.8	71		1.1		0.70		3.0	33		23
C18128		58	90		1.2		27		12	71		68
C18129		23	88		1.6		6.8		20	50		61
C18130		260			6.7		150		29	31		64
C18552	0.05	6.0	170	80	0.80	8.0	0.35	12	3.2	61	0.88	19
C18553	0.02	2.0	61	40	0.81	26	<0.10	7.0	2.1	28	0.90	5.0
C18554	0.02	7.0	180	60	0.75	5.0	<0.10	9.0	2.7	26	0.80	7.0
C18555	0.04	2.0	200	80	0.75	9.0	<0.20	11	3.3	31	1.5	9.0
C18556	0.03	3.0	150	150	0.85	7.0	<0.10	28	3.2	30	2.7	8.0
C18557	0.12	50	82	170	1.9	66	1.6	130	7.0	62	2.6	19
C18669	0.02	1.0	5.0	190	0.67	7.0	<0.10	33	7.5	17	2.1	19
C18670	0.01	0.50	2.0	180	0.67	2.5	<0.10	26	7.8	11	0.30	15
C18879	0.01	0.50	1.0	180	0.56	2.3	<0.10	21	5.1	10	0.88	11

TABLE 20—Continued

SAMPLE	[illegible]	[illegible]	B	BA	BE	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.01	0.50	1.0	200	0.61	1.5	<0.10	55	[illegible]	[illegible]	1.5	[illegible]
[illegible]	0.20	5.0	2.0	300	0.50	1.5	0.20	67	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.05	11	20	600	1.0	0.50	0.50	100	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.03	11	12	100	1.0	25	<0.10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.02	11	16	190	1.0	29	<0.10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.02	1.0	5.0	150	1.0	28	<0.10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.01	2.0	8.0	110	1.1	27	<0.10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.02	5.0	10	190	0.94	30	<0.10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.06	6.0	16	200	1.0	25	0.20	50	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.10	60	27	120	2.5	5.0	0.50	50	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.07	5.0	100	50	0.64	8.0	<0.50	5.0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.02	6.0	65	50	0.60	15	<0.10	7.0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.08	1.0	62	50	0.35	7.0	<0.10	5.0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.01	2.0	90	90	0.88	6.0	<0.10	6.0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.01	6.0	120	60	1.0	7.0	<0.10	7.0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.02	7.0	70	60	1.5	6.0	0.20	5.0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.05	15	10	230	1.5	6.0	0.50	40	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	0.07	0.50	30	200	0.61	1.5	<0.10	5.0	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	<0.01	0.50	92	250	0.36	1.5	<0.10	7.0	0.70	[illegible]	[illegible]	[illegible]
[illegible]	0.01	1.0	30	260	0.55	6.0	<0.10	[illegible]	0.70	[illegible]	<0.01	[illegible]
[illegible]	0.03	2.0	24	500	0.90	5.0	<0.10	20	0.60	[illegible]	[illegible]	[illegible]
[illegible]	0.05	11	35	390	0.60	1.5	<0.80	25	[illegible]	[illegible]	[illegible]	11
[illegible]	0.02	2.0	41	500	0.48	1.2	<0.10	10	1.0	5.0	0.00	10

NOTE: Samples listed by sample number (C-number). Refer to table 19 for identification of samples.

TABLE 20--Continued

SAMPLE	DY	EU	F	GA	GE	HF	HG	I	IN	LA	LU	MN
C18090				1.5	8.0		0.29					40
C18093				1.1	2.0		0.06					8.0
C18095				3.3	10		0.11					6.0
C18096				3.3	7.0		0.01					10
C18097				6.5	6.0		0.15					15
C18098				3.8	4.0		0.29					28
C18099				1.7	4.0		2.1					81
C18106				9.9	5.0		0.70					
C18107				2.1	1.3		2.9					55
C18094				3.0	6.0		0.62					13
C18100				3.7	10		0.07					8.0
C18101				3.1	6.0		4.0					24
C18111				2.1	88		0.26					26
C18114				2.2	30		0.29					68
C18115				2.3	30		0.08					6.0
C18116				1.8	21		0.13					6.0
C18117				4.80	23		0.21					6.0
C18118				1.5	21		0.19					12
C18119				5.1	15		0.38					26
C18140				12	12		1.2					210
C18141				2.0	8.0		1.6					
C18142				1.1	8.0		9.6					85
C18121				5.7	4.0		0.19					88
C18122				9.0	11		0.17					130
C18123				2.1	13		0.17					7.0
C18124				0.70	17		0.08					8.3
C18125				2.8	13		0.09					10
C18126				1.2	10		0.13					16
C18127				5.2	6.0		0.17					26
C18128				12	1.0		0.88					270
C18129				15	1.0		0.77					560
C18130				2.5	1.0		3.8					78
C18562	0.70	0.21		6.0	0.50	0.50	0.23			11	0.21	210
C18563	0.50	0.15		3.0	4.1	0.30	0.24			2.3	0.05	12
C18564	1.1	0.28		6.0	0.75	0.50	0.13			4.8	0.05	2.1
C18565	1.0	0.27		8.0	0.10	0.70	0.18			5.8	0.10	80
C18566	1.2	0.34		8.0	0.20	1.1	0.17			17	0.10	45
C18567	1.1	0.60		17	1.1	1.6	0.51			22	0.22	190
C18869	1.7	0.50		7.0	0.10	1.8	0.09			15	0.13	26
C18870	1.9	0.30		5.0	0.25	0.80	0.03			12	0.07	1.2
C18871	1.8	0.37		5.0	0.28	1.0	0.08			18	0.08	2.8

TABLE 20—Continued

SAMPLE	DY	EU	F	GA	GE	HF	HG	I	IN	LA	LU	ND
[illegible]	4.0	0.52		6.0	0.10	1.6	0.03			17	0.18	7.6
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	<0.10	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	<0.10	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	<0.10	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	0.70	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	0.70	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
C19009	0.50	[illegible]		1.0	<0.10	0.50	[illegible]			[illegible]	[illegible]	[illegible]
C19010	0.80	[illegible]		1.0	<0.10	0.80	[illegible]			[illegible]	[illegible]	[illegible]
C19011	0.80	[illegible]		[illegible]	<0.10	1.1	[illegible]			[illegible]	[illegible]	[illegible]
C19012	1.1	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
C19013	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	[illegible]
C19014	0.70	0.12		2.0	<0.10	0.90	0.06			6.0	0.08	6.6

NOTE: Samples listed by sample number (C-number). Refer to table 19 for identification of samples.

TABLE 20—Continued

SAMPLE [illegible]

TABLE 20--Continued

SAMPLE	MO	NI	P	PB	RB	SB	SC	SE	SM	SN	SR	TA
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

NOTE: Samples listed by sample number (C-number). Refer to table 19 for identification of samples.

TABLE 20--Concluded

SAMPLE	TB	TH	TL	U	V	W	YB	ZN	ZR
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

NOTE: Samples listed by sample number (C-number). Refer to table 19 for identification of samples.

TABLE 21.--MAJOR AND MINOR ELEMENTS IN LABORATORY-PREPARED WASHED COAL SAMPLES

(percent, moisture-free whole coal basis)

SAMPLE	AL	CA	CL	FE	K	MG	NA	SI	TI
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 13—PROXIMATE ANALYSES OF LABORATORY-PREPARED WASHED COAL SAMPLES
(percent of whole coal except for Btu values)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]				
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

NOTE: Refer to table 1 for abbreviations; refer to table 10 for identification of samples.

TABLE 23.—ULTIMATE ANALYSES OF LABORATORY-PREPARED WASHED COAL SAMPLES

(percent, moisture-free whole coal basis)

NOTE: Refer to table 1 for abbreviations; refer to table 15 for identification of samples.

TABLE 2-—SULFUR ANALYSES OF LABORATORY-PREPARED WASHED COAL SAMPLES
(percent, moisture-free whole coal basis)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]		[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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NOTE: Refer to table for abbreviations; refer to table [illegible] for identification of samples.

Displaying Washability Data

The float-sink, or washability, data can be displayed as washability curves and as histograms. Washability curves and histograms for a series of elements are shown in figures 69 through 74. The figures are presented in order of increasing tendencies of the elements to be concentrated in the heavier fractions (decreasing organic affinity). The washability curve is a type of cumulative curve from which the expected concentration of an element at any given recovery rate of a coal can be read assuming the separation was based on specific gravity differences. Therefore, the abscissa is "recovery of float coal in percent" and should be applicable to any specific gravity separation without regard to the medium in which it is done or the method used. The raw coal concentration of an element is read at the 100-percent recovery point; the concentration in the cleanest coals (most free of mineral matter) is read at the low recovery end of the curve (20 to 30-percent recovery).

Figure 69 shows the washability curve and the histogram for germanium in a sample from the Davis Coal Member. The negative slope of the curve indicates that germanium is concentrated in the clean coal fractions. This is also apparent from the histogram. The histogram also indicates that there is higher concentration of germanium in the 1.60 to >2.79 specific gravity fraction than in the >2.79 specific gravity fraction. Apparently, a greater portion of the germanium is concentrated with the clay minerals than with the sulfide minerals that compose the majority of the >2.79 sink fraction.

An element that is uniformly distributed in the various fractions of the washed coal will have a washability curve with a slope of zero (flat); washing such a coal will have no effect on the concentration of the element in the clean coal. An example of this type of distribution is shown by the washability curve and histogram of bromine for a sample from the Pittsburgh No. 8 coal in West Virginia (fig. 70).

A positive slope of the washability curve shows that the element is concentrated in the inorganic (mineral matter) portion of the coal. The more strongly associated the element is with the inorganic fraction, the steeper is the slope of the curve. Washability data on Cr in a sample from the Blue Creek coal in Alabama give a washability curve with a positive slope but the curve does not approach the origin (fig. 71), rather when extended the curve intercepts the ordinate at approximately 10 ppm.

A curve with a steeper positive slope is obtained when the washability data for As in the same coal (Blue Creek seam, Alabama) are plotted (fig. 72). Apparently, arsenic is more strongly associated with the mineral matter fraction of the coal than is chromium. We would expect that it is present in solid solution in the iron sulfide minerals.

The washability curve for the low-temperature ash of a sample from the Pocahontas No. 4 seam in West Virginia is shown in figure 73. This coal washes readily to produce a relatively "clean" coal with fairly high recovery. Elements such as arsenic, which have washability curves that are steeper than that for the low-temperature ash (LTA) are even more easily removed by washing than is the "average" ash.

Sulfur is present in coals in both organic and inorganic combination; the standard analyses report the varieties of sulfur as sulfate sulfur, pyritic sulfur, and organic sulfur. In a sample from the Herrin (No. 6) Coal in Illinois, the washability curve for total sulfur shows the contribution from both organic and inorganic sulfur (fig. 74). The sulfur content decreases rather rapidly in the washed coal as that part that is concentrated in the heavier mineral-matter-rich portion (inorganic sulfur) is removed, but then the curve flattens because the lighter coal fractions also contain appreciable amounts of sulfur (organic sulfur).

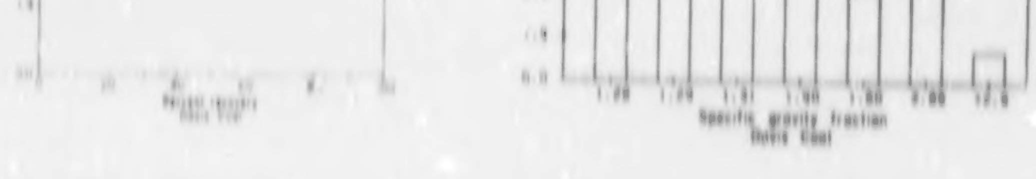

Fig. 69 - Germanium in specific gravity fractions of a sample from the Davis Coal Member. Left: washability curve. Right: distribution of germanium in individual fractions.

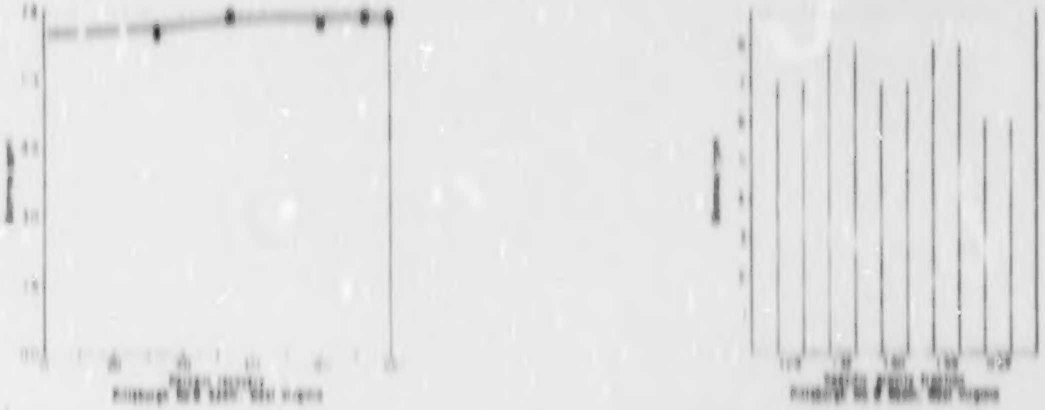

Fig. 70 - Bromine in specific gravity fractions of a sample from the Pittsburgh No. 8 coal from West Virginia. Left: washability curve. Right: distribution of bromine in individual fractions.

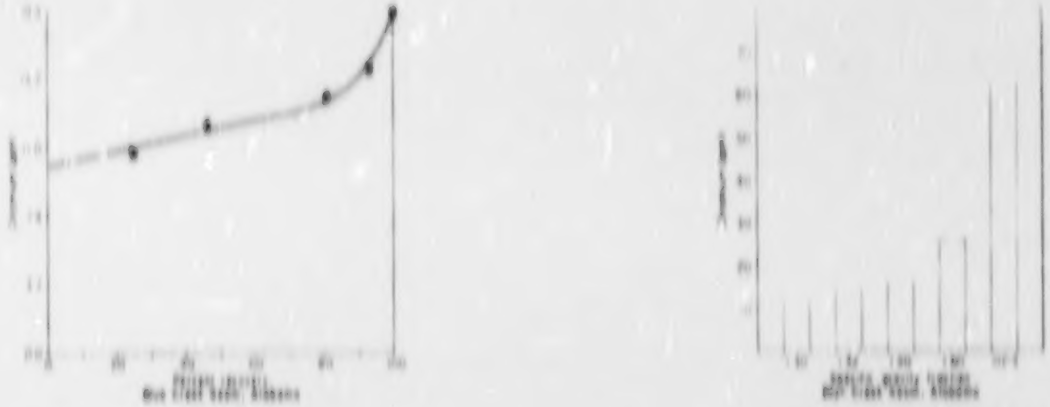

Fig. 71 - Chromium in specific gravity fractions of a sample from the Blue Creek coal from Alabama. Left: washability curve. Right: distribution of chromium in individual fractions.

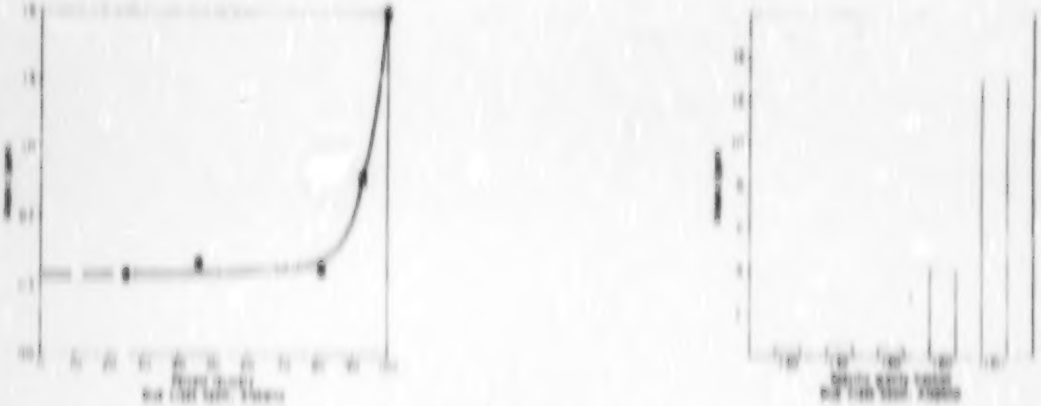

Fig. 72 - Arsenic in specific gravity fractions of a sample from the Blue Creek coal from Alabama. Left: washability curve. Right: distribution of arsenic in individual fractions.

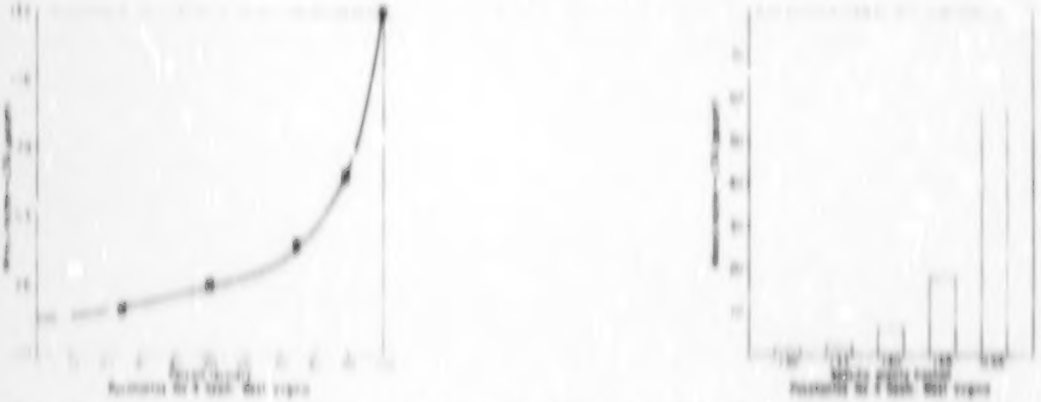

Fig. 73 - Low-temperature ash in specific gravity fractions of a sample from the Pocahontas No. 4 coal from West Virginia. Left: washability curve. Right: distribution of low-temperature ash in individual fractions.

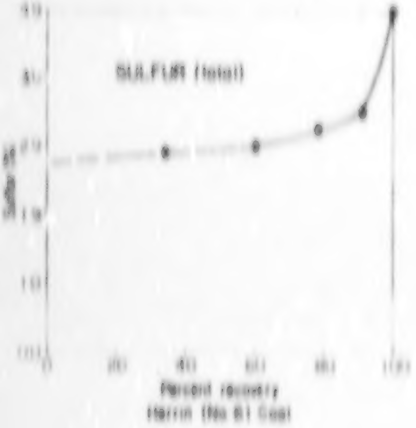

Fig. 74 - Washability curve of sulfur in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member.

ORGANIC AND INORGANIC AFFINITIES OF THE ELEMENTS

Introduction

Washability curves and histograms of washability data are effective means of depicting the mode of combination of elements in coal; they indicate whether the elements are associated with the organic or inorganic fractions of the coal. However, more than 350 sets of washability curves and histograms would be needed to display the washability data given in tables 20 through 24. Therefore, we have attempted to quantify the information presented on the curves and have produced an "organic affinity" index.

The concept of an organic or inorganic affinity for elements in coal is not original in this report. Dr. V. M. Goldschmidt, who pioneered modern investigations of trace elements in coals, identified trace elements in inorganic combination with minerals in coals. He also postulated the occurrence of metal organic complexes in coal; the observed concentrations of vanadium, molybdenum, and nickel were attributed to the presence of such complexes (Goldschmidt, 1935).

Nicholls (1968) approached this problem by plotting the analytical data for the concentration of a single element in coal or in coal ash against the ash content of the coal. Diagrams depicting a number of such points for a single coal seam, or for a group of coal seams in a single geographic area, were interpreted for degree of inorganic or organic affinity of the element. Nicholls concluded (1968, p. 283):

> "...one element, boron, is largely, almost entirely, associated with the organic fraction in coals; some elements, such as barium, chromium, cobalt, lead, strontium, and vanadium are, in the majority of cases, associated with the inorganic fraction; and a third group including nickel, gallium, germanium, molybdenum, and copper, may be associated with either or both fractions."

Nicholls then subdivided the third group into nickel and copper, which are in inorganic combination when found in large concentrations, and into gallium, germanium, and molybdenum, which are largely in organic combination when found in large concentrations.

Horton and Aubrey (1950) handpicked pure vitrain samples from coals and separated the samples into five different specific gravity fractions. They then analysed these fractions for 16 minor elements. They concluded that for the three vitrains that were studied, beryllium, germanium, vanadium, titanium, and boron were contributed almost entirely by the inherent (organically combined) mineral matter and that manganese, phosphorus, and tin were associated with the adventitious (inorganically combined) mineral matter.

A much more ambitious series of investigations of the organic-inorganic affinities of trace metals in coals were undertaken and were reported on by Zubovic and co-workers at the U.S. Geological Survey (Zubovic, 1960, 1966, 1976; and Zubovic et al., 1960, 1961). In the more recent of these articles Zubovic (1966, 1976) listed the following 15 elements in decreasing order of percent organic affinity: Ge (87); Be (82), Ga (79), Ti (78), B (77); V (76); Ni (59), Cr (55); Co (53); Y (53), Mo (40), Cu (34), Sn (27); La (3); and Zn (0).

Zubovic (1976, p. 50) then related the ranking of the elements in the table of organic affinity to the complexing ability of the metals with organic ligands; he suggested that the metals having high organic affinities in coal are present as chelates.

Ruch, Gluskoter, and Shimp (1974) and Gluskoter (1975) published tables of organic affinities for 21 elements determined on four samples of Illinois coals that had been washed in the laboratory. The elements were listed in decreasing order of organic affinity, but numerical values were not given for the index. The analytical results on which those organic affinities were based are included in tables 20 through 24. Washability data for up to 53 elements and 10 coal parameters from five additional coals are also included in those tables.

Calculation of Organic Affinities

The washability data are summarized in table 25 and numerical values for organic affinity have been assigned. The value for the organic affinity index for a specific element is obtained by calculating the area beneath the washability curve. This calculation is done on a curve that has been drawn to a predetermined and constant scale (normalized) and on a curve which has been adjusted for that part of the mineral matter that is inseparable from the lightest coal fraction.

The curves are normalized by calculating a scale factor then multiplying the ordinate values by that factor. The scale factor is obtained by dividing the value at 100 percent recovery (V) by the number of centimeters in the Y axis. V is not necessarily the maximum value. A unit area is obtained by determining the area (in square centimeters) of the square formed by the points (0,0), (0,V), (100%,V), and (100%,0). To normalize the curve, the area under the curve is divided by the area of the square.

Examples of "standard" and "adjusted" washability curves are given in figures 75, 76 and 77. These three sets of curves were chosen to demonstrate the method of calculating organic affinities and to provide a visual basis for comparison of the numerical values of organic affinities in table 25.

Both unadjusted (standard) and adjusted, normalized washability curves for zinc in a sample of Herrin (No. 6) Coal are given in Figure 75. In the standard (unadjusted) washability curve the extrapolated ordinate intercept is approximately 4.5 ppm. The adjusted curve intercepts the ordinate at zero and the curve reaches the zero zinc value at approximately 90 percent recovery (90 on the abscissa). The adjusted cumulative curve was constructed after the following value, "F," was subtracted from each of the 5 datum points used in the calculation:

$$F = \frac{\text{LTA(Light)}}{\text{LTA(1.60 S)}} \times \text{Zn(1.60 S)} = \frac{6.10}{77.80} \times 250 \text{ ppm} = 19.6 \text{ ppm}$$

LTA (Light) is percent low-temperature ash in the lightest float fraction.

LTA (1.60 S) is percent low-temperature ash in 1.60 sink fraction.

Zn (1.60 S) is zinc concentration in 1.60 sink fraction (ppm)

If the value of a datum point is negative after "F" is subtracted from the reported concentration, the value is then taken to be zero.

A fourth order polynomial curve is drawn to best fit the data points and the area under the curve is calculated. The entire normalized area of the graph is defined as the value "1.00." An element which is removed, to any degree, from the clean coal fraction by washing the coal has a value less than 1.00; for example, see Zn in figure 75. The organic affinity of zinc in that sample is 0.08, an extremely low value, indicating that the element is present almost entirely in the mineral matter fraction.

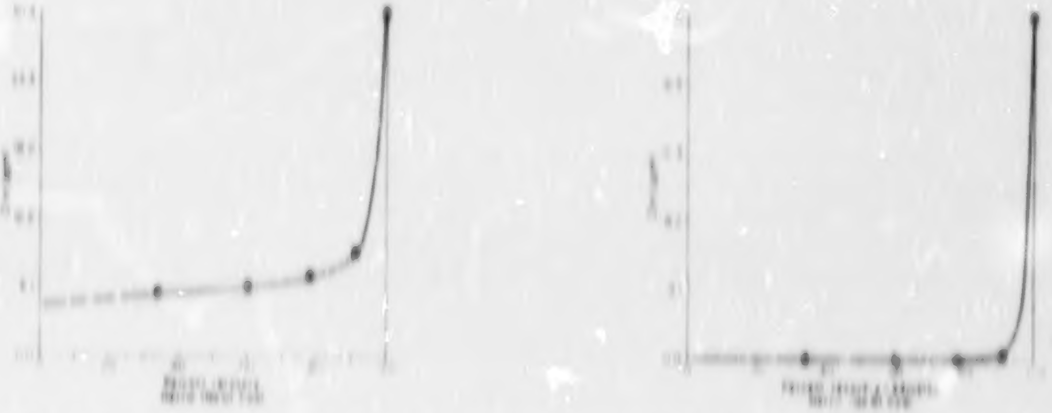

Fig. 75 - Washability curves for zinc in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member. Left: standard washability curve. Right: adjusted washability curve.

It is possible for an element to have an organic affinity greater than 1.00, as in the case for bromine in a sample of the Blue Creek Coal from Alabama (fig. 76). Both standard and adjusted washability curves for Br are shown in figure 76. The lighter specific gravity fractions of the coal contain larger amounts of Br than the heavier fractions rich in mineral-matter. Bromine is an element which generally has a high organic affinity index—in this case 1.20. Standard and adjusted curves are nearly identical, inasmuch as there is only a minor contribution from the inseparable mineral matter to the total bromine content. The organic affinity index is an open-ended scale. The upper limit is only dependent upon the difference between the extrapolated Y intercept and V (the concentration of the element in the coal prior to washing).

A number of metals have washability curves intermediate between those elements that are generally concentrated in the inorganic fraction (such as zinc) and those that are concentrated in the organic fraction (such as bromine). Washability curves for copper, both standard and adjusted, are given for a sample of coal from the Davis bed in Illinois in figure 77. The adjusted curve intersects the ordinate at a lower value than does the standard curve. But even with the removal of a hypothetical amount of copper contained in the inseparable minrral matter there is still an appreciable amount of copper left in the cleanest coal fractions. The organic affinity of copper in this sample is 0.56.

Discussion of Organic Affinities

Organic affinities for most of the determined elements are given for eight sets of washed coal samples in table 25. Four of the samples are from the Illinois Basin, three are from the Appalachians, and one is from Arizona. One sample from the Illinois Basin is not included in the table of organic affinities (table 25) because the sample was separated into only two fractions, and organic affinities could not be calculated on those limited data.

Organic affinities have not been calculated for all of the elements determined because the concentrations of a few elements in some of the washed fractions were below the limits of accurate detection. The concentrations of the elements in the whole sample, as calculated from the recombination of the concentrations in the washed fractions, are also given in table 25.

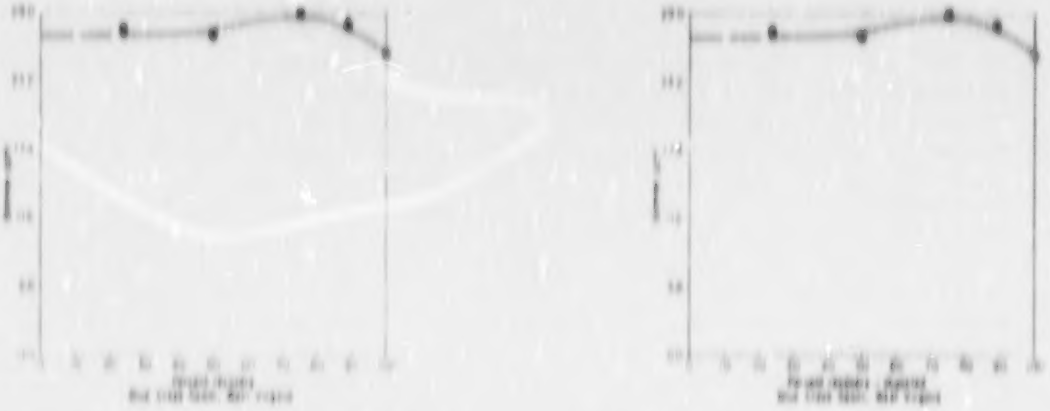

Fig. 76 - Washability curves for bromine in specific gravity fractions of a sample from the Blue Creek coal from Alabama. Left: standard washability curve. Right: adjusted washability curve.

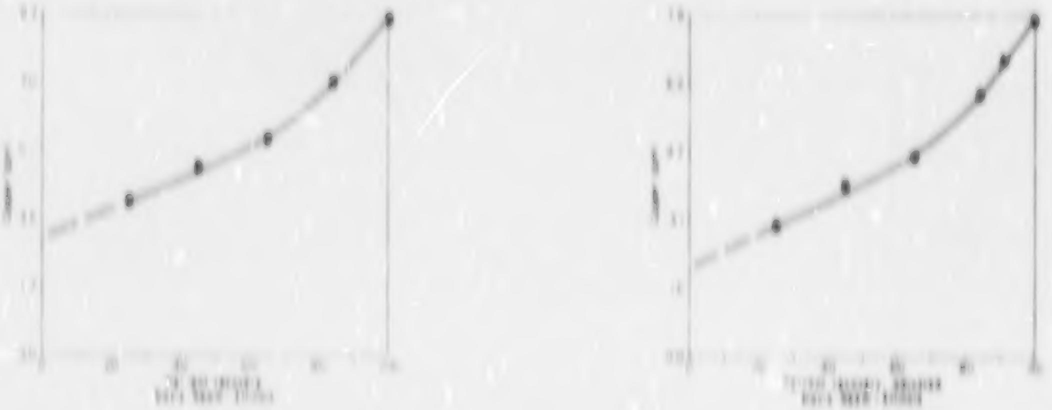

Fig. 77 - Washability curves for copper in specific gravity fractions of a sample from the Davis Coal Member. Left: standard washability curve. Right: adjusted washability curve.

Varieties of sulfur (pyritic sulfur, organic sulfur, and sulfate sulfur) as well as total sulfur have been determined on all fractions of the washed coal samples. Content of sulfate sulfur is very low and generally does not make a significant contribution to the total sulfur content of a fresh coal sample. If the analyses for varieties of sulfur were precise and accurate, if our measurements of the amount of coal in each washability fraction were accurate, and if the measurements of the amount of low-temperature ash were accurate, we would then expect a perfect correlation between organic affinity of total sulfur and percent of organic sulfur in the total sulfur. This relationship is shown for eight coals in figure 78. The agreement is good and is well within the analytical error for determining those factors mentioned above. We were fortunate because the sample set analysed has a wide range of organic affinities for total sulfur (0.12 to 1.08) and the organic sulfur contribution to the total sulfur content also has a wide range (22 percent to 92.5 percent).

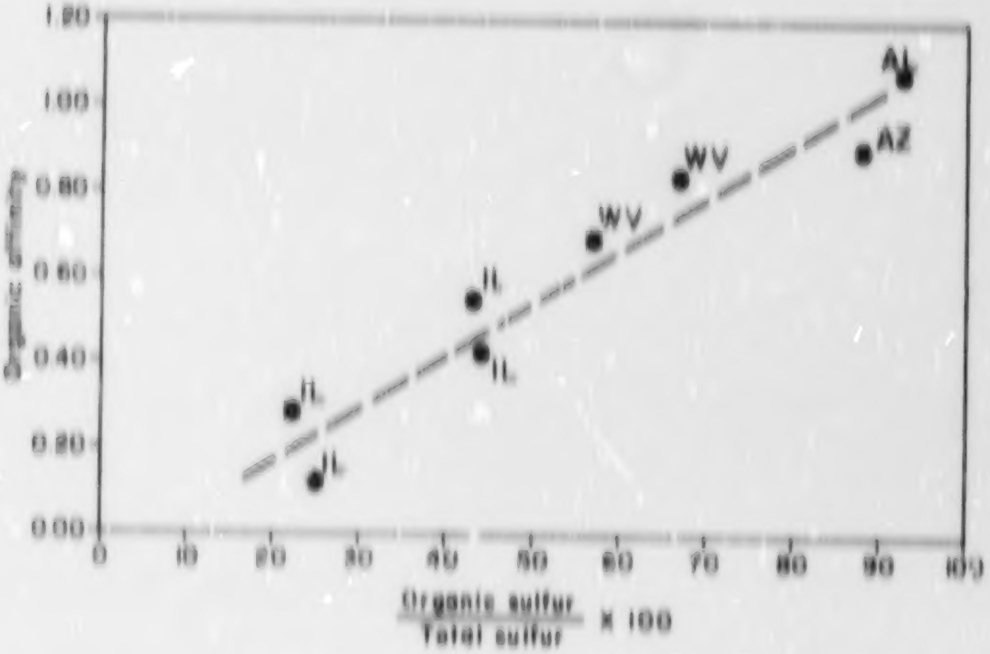

Fig. 78 - Organic affinity index for total sulfur and ratio of organic sulfur to total sulfur in eight washed coal samples.

On the basis of the calculated organic affinities, the elements in each of the eight samples may be divided into four groups: organic, intermediate-organic, intermediate-inorganic, and inorganic. They are listed in these groups in table 26. The elements were placed in these groups in a somewhat arbitrary manner and not strictly on the basis of the value for organic affinity. The actual values that lie immediately above and below the cutoff points for the different categories are shown. In general, the groups are divided as follows: organic, greater than 0.67; intermediate-organic, 0.50 through 0.66; intermediate-inorganic, 0.34 through 0.49; and inorganic, less than 0.33.

The four coals from the Illinois Basin are much more similar to each other with regard to organic affinities than they are similar to the coals from other areas. The following are generalizations applicable to the four samples of Illinois coals:

1. Ge, Be, B, and Sb are classified within the organic group in all samples.

2. Ge has the highest organic affinity in each case.

3. Zn, Cd, Mn, As, Mo, and Fe are in the inorganic group in all four samples.

4. Zn and As have consistently the lowest values observed (0.08 to 0.09).

5. A number of metals including Co, Ni, Cu, Cr, and Se are intermediate in value. This characteristic suggests a partial contribution from sulfide minerals in the coal, but also suggests the presence of organometallic compounds that contain these elements, or the presence of chelated species and/or adsorbed cations.

The number of generalizations decreases when organic affinities from the three coals from Appalachia and the one coal from Arizona are considered.

1. Be, Ge, and B are among the elements with higher organic affinity in most of the cases. However, Ge has an organic affinity of 0.10 (very inorganic) in the sample from Arizona and B is relatively inorganically combined in the sample from Alabama (organic affinity = 0.32).

2. Bromine was determined in one sample of the Herrin (No. 6) Coal from Illinois and in the four samples from outside the Illinois Basin. The organic affinity for Br was placed in the "organic" group in all five coals.

(Text continued on page 118)

TABLE 25--ORGANIC AFFINITY OF PARAMETER DETERMINED IN LABORATORY-PREPARED WASHED COAL SAMPLES

	Float-Sink Set 1			Float-Sink Set 2			Float-Sink Set 3			Float-Sink Set 4		
	R	A	C	R	A	C	R	A	C	R	A	C
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

NOTE: "R" = ranking of parameter by organic affinity.
"A" = calculated organic affinity.
"C" = concentration of parameter at 100 percent recovery (a calculated raw coal basis).
See table 1 for other abbreviations.

TABLE 25—Concluded

	Float-Sink Set 5			Float-Sink Set 6			Float-Sink Set 8			Float-Sink Set 9		
	R	A	C	R	A	C	R	A	C	R	A	C
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

NOTE: "R" = ranking of parameter by organic affinity.
"A" = calculated organic affinity.
"C" = concentration of parameter at 100 percent recovery (a calculated raw coal basis.)
See table 1 for other abbreviations.

TABLE 26—ORGANIC AFFINITY OF ELEMENTS IN LABORATORY-PREPARED WASHED COAL SAMPLES

Float-Sink Set 1		Float-Sink Set 2		Float-Sink Set 3		Float-Sink Set 4		
Ge U Br V Cr Be Dy	.85	Br Ge Co B Ni V Cu Dy Sr Be Y La U	.72	Co Br Ni Sr Be P W Mo Cr P Fe	.61	Sr Br B U Be P S Bi Gd	.82	Organic
Cr B Ni Co Cu Be Lu Yb B Sc	.80 .55	Pb Sm Yb Eu Nd Ce Tb Dy P	.67 .55	Pr Tb Eu Cu V Gd Tb Ce Sn Lu Ga	.70 .60	Pb Bi Mo Ni Co Gd Ce V	.71 .57	Intermediate-Organic
Th Sr Hf W Yb Fe U La Eu Sm	.59 .38	Cr Sr Be Yb Ti Sm Lu Pr Hf Th Al	.60 .35	Co Sc Mo K Nd Ge La Mn U Cr Pb Mg	.60 .37	Cu Mg La Sm Ni Eu Nd Sn Mn Cr Ce Sc Zn Yb	.65 .31	Intermediate-Inorganic
Pb Sm Al Si Mg LTA Sn Ba Cs Cd Sr Co Fe Mn As La P Zn Ca	.28	Ta K Cs Zn Na LTA Si S Mg Cd Rb Mn As	.33	Hg Ti Ta Th Hf Al Sr LTA Ca Rb Si K Zn	.32	Sb Al Fe Hf Lu Sr As Ta Th LTA Ba K Cs Cd Si	.31	Inorganic

TABLE 26—Concluded

Float-Sink Set 5		Float-Sink Set 6		Float-Sink Set 8		Float-Sink Set 7		
B Na P Hg [illegible] Fe S Ni Co Br Sr Ca [illegible] Ag Yb Lu V Lu Sb	 .66	Ge B Ge P [illegible] [illegible] Cr	 .68	Ge P Na B Ga	 .61	Ge B [illegible] [illegible]	 .69	Organic
[illegible] Ce [illegible] La Eu Cr Yb U Mn W	.63 .51	Cu [illegible] [illegible] Ni S V	.66 .50	Sb Co [illegible] Na V B Ni	.68 .51	Y U [illegible] Mo	.66 .52	Intermediate-Organic
B Sm Hf Sr Ta Al Th Ga	.50 .25	Al Cu Si Mn	.50 .30	Pb Cu Si Al Cr C Hg	.50 .20	Na Mo Ni Cr Co Hg Cu	.50 .25	Intermediate-Inorganic
Sb Ti Mn Hg LTA As Si Pb Cd Ge	.25	Zr LTA S As Cd Hg Mn Pb Zn Fe	.26	Fe LTA As Mo Cd Cr Cu Zn Ca	.22	P Ti Fe Sr K LTA Al Si As Pb Cd Mn Zn Ca	.18	Inorganic

NOTE: Grouped in 4 categories: organic, intermediate-organic, intermediate-inorganic, inorganic. Values for the indices of organic affinity separating classes are indicated.

3. Arsenic is the only one of the usually inorganic elements that was classified in the inorganic group in all of the coal samples studied.

4. Cesium was not determined in all samples. However, cesium was among the elements with the lowest organic affinities in four of five samples in which it was determined. It was in the intermediate-organic group in the fifth sample.

5. Uranium was classed among the organic elements in three of the five washed coal samples in which it was determined and was in the intermediate categories in the remaining two sets.

The observed relationships of the elements, as expressed by their organic affinities, have not suggested any geochemical anomalies. The elements grouped as "organic" are those that are often found in organic combination in natural materials. These elements include several that have been identified in organic combination in coals by previous workers (Horton and Abernathy, 1950; Ratynskiy et al., 1966; Zubovic, 1966, 1976). Also, a number of elements that have not generally been determined on coal samples in the past have been determined, reported upon, and are included in the table of organic affinities. Examples of such elements include the lanthanides and the rare earths.

The elements grouped as "inorganic" are those that have been identified in coals in discrete mineral phases: As, Zn, Cd, and Fe, as sulfides; and Mn, in carbonates. Although Cs has not been identified directly in coal, it is generally readily adsorbed in the atomic lattice of clay minerals and presumably is present in the coals in this manner.

It is significant that we cannot make many generalizations on the basis of the analyses of eight coals from the three widely separated areas: the Appalachian Basin, the Illinois Basin, and Arizona. If information is desired on the mode of occurrence of elements in a particular coal sample, it will probably be necessary to separate that coal into specific gravity fractions and to analyse it for those elements, or to otherwise make those determinations. On the basis of the five sets of washability samples analysed from Illinois, an estimate of the organic and inorganic affinities of the elements in other coals from the Illinois Basin is likely to be more accurate than a similar estimate made on coals from outside of the area.

Although an element may be listed among those with the highest organic affinities, its occurrence in inorganic combination in coals is not precluded. Boron, which is among those found in high concentrations in the cleanest coal fractions, is known to occur in amounts up to 200 ppm in the clay mineral illite from Illinois coals (Bohor and Gluskoter,1973). Similarly, a portion of those elements usually concentrated in the high specific gravity fractions (low organic affinity) may also be in organic combination.

Concentration of an element in the heavier fractions shows that element to be in inorganic combination. In the cases in which the final separation was done in bromoform (2.89 s.g.), we can postulate further on the mode of occurrence of certain elements. Si, Ti, Al, and K are concentrated in the gravity fraction from 1.60 to 2.89 and are less abundant in the gravity fraction greater than 2.89. These elements are found associated with each other in the clay minerals, but not in the heavier sulfide minerals.

SUMMARY AND CONCLUSIONS

Extensive chemical analyses on 172 "whole coal samples", 40 "bench" samples and 64 "washed" coal samples have been done at the Illinois State Geological Survey. As many as 71 determinations have been made on a single sample. Analytical methods used were: atomic absorption spectroscopy (flame and graphite furnace), neutron activation analyses (instrumental and with radio-chemical separations), optical emission spectrometry (direct reader and photographic), X-ray fluorescence spectrometry (wavelength dispersive and energy dispersive), and ion selective electrode analyses. Discussions of the analytical methods are given in the Appendix.

Chemical elements determined are Al, Sb, As, Ba, Be, B, Br, Cd, Ca, C, Ce, Cs, Cl, Cr, Co, Cu, Dy, Eu, F, Ga, Ge, Au, Hf, H, In, I, Fe, La, Pb, Lu, Mg, Mn, Hg, Mo, Ni, N, O, P, K, Rb, Sm, Sc, Se, Si, Ag, Na, Sr, S, Ta, Tb, Tl, Th, Sn, Ti, W, U, V, Yb, Zn, and Zr. Normal coal parameters reported on the samples are moisture, low-temperature ash, high-temperature ash, total sulfur, sulfate sulfur, organic sulfur, pyritic sulfur, calorific value, free-swelling index, Gieseler plasticity, water soluble chlorine, proximate analyses, and ultimate analyses.

Of the 172 whole coal samples analysed, 114 are from the Illinois Basin, 29 are from coal areas in western United States, 23 are from eastern (Appalachian) coal fields, 4 are from midcontinent coals, and the remaining two are "standard" coal samples. Statistical analyses of the chemical data elicited a number of observations including the following:

1. Elements that have relatively large ranges in concentration and that have standard deviations larger than the arithmetic means (for example, As, Ba, Cd, I, Pb, Sb, and Zn) include those that are found in coals within sulfate

and sulfide minerals or those that would be expected to be found in that association. Elements that occur in organic combination or that are contained within the silicate minerals have narrow ranges and smaller standard deviations. Many of the silicate minerals are thought to be emplaced in the coal very early in the period of coal formation as detrital or as syngenetic minerals. The sulfides and some sulfates, although syngenetic in part, have a major portion emplaced in the coal by epigenetic mineralization.

2. In general, elemental concentrations tend to be highest in coals from eastern United States, lowest in coals from western United States, and intermediate in value in coals from the Illinois Basin.

3. Many elements are positively correlated with each other in coals. The most highly correlated are Zn:Cd (r = 0.96 for coals of the Illinois Basin). Chalcophile elements (As, Co, Ni, Pb, and Sb) are all mutually correlated, as are the lithophile elements (Si, Ti, Al, and K). Other significant correlations are Ca:Mn (r = 0.65) and Na:Cl (r = 0.48).

The average concentration of an element in the earth's crust is its clarke value. The geometric mean value for each minor and trace element was compared to the clarke for that element. Only four of the elements determined were enriched in the coals by a factor of six or more relative to the clarke. Boron, chlorine, and selenium are enriched in coals of the Illinois Basin; arsenic, chlorine, and selenium are enriched in coals of eastern United States; and selenium is the only element enriched in coals of western United States.

The enrichment of selenium in coals may represent a contribution from the plants that formed the coal. Selenium occurs in amounts well in excess of the clarke in all coals analysed and has been reported in like amounts in modern peats. Boron has been used as an indicator of paleosalinity in sedimentary rocks. It is concentrated relative to the clarke only in the coals of the Illinois Basin and probably represents a higher salinity of the waters in the coal swamp or of the waters that covered the peat as the swamp was drowned.

Only four elements were found to be enriched in coal by a factor of six times the clarke or greater. A larger number of elements are depleted in coals (one-sixth the clarke value or less). Those elements depleted in coals of the Illinois Basin are: Al, Ca, Cr, F, Hf, K, Lu, Mg, Mn, Na, P, Sc, Si, Sr, Ta, and Ti. All of the other elements determined are within the range of one-sixth to six times the clarke.

A series of five sample sets (40 samples) was collected by sampling the coal seam in vertical segments or benches. All five of the bench sets were from the Herrin (No. 6) Coal Member in Illinois. Elemental distributions were quite variable within bench sets, although the rare earth elements and bromine tended to be more uniformly concentrated.

Elements often concentrated in the top or bottom benches of the coal include U, Mo, V, Sb, and Ge. The concentration of Ge in the top and bottom benches of four of the five bench sets analysed is striking. This concentration and the demonstrated affinity of germanium for the organic portion of the coal suggest that the germanium was introduced into the coal seam after burial by circulating solutions. Those solutions were necessarily in contact with the horizontal boundaries of the coal seam before the center parts of the seam; the change in geochemical conditions at those boundaries allowed for the assimilation of the germanium by the coal.

Rock units immediately associated with the coals (roof shales, underclays, and partings) were analysed with some of the bench sets. Most elements are found in significantly higher concentrations in these rock units than in the coals. Those elements include: Ag, Ba, Cd, Co, Cr, Cs, Cu, F, Ga, Hf, La, Mn, Sc, Se, Sm, Sr, Th, V, Yb, Zr, K, Mg, Si, Na, and most of the rare earth elements.

Nine coal samples were separated into specific gravity fractions (washed) and were analysed for most of the major, minor, and trace elements, as were the 172 whole coals. A total of 64 washed samples were studied. Five of the washed coals were from the Illinois Basin, three were from widely separated areas in eastern coal fields, and one was from Arizona. The float-sink or washability data for the elements may be shown as washability curves and as histograms. The mode of occurrence of an element, whether it is inorganically or organically combined in the coal, may be interpreted from the washability curves.

A value for the organic affinity of the elements has been defined by normalizing the washability curves, removing from them a component that represents the contribution from the inseparable mineral matter, and then calculating the area under the washability curve. This value ranges from 0.08 to 2.02 for the elements determined in the coals analysed.

Elements within a single washed coal set of analyses are placed in one of the following four groups: 1) organic, 2) intermediate-organic, 3) intermediate-inorganic, and 4) inorganic. The four samples from the Illinois Basin on which these organic affinities were calculated are quite similar to one another; several generalizations can be made from them:

1. Ge, Be, B, and Sb are classified in the organic group in all samples; Ge has the highest organic affinity in all four instances.

2. Zn, Cd, Mn, As, Mo, and Fe are in the inorganic group in all four samples; Zn and As consistently have the lowest values.

3. A number of metals including Co, Ni, Cu, Cr, and Se, have organic affinities that place them in the intermediate categories. This suggests that these metals are present in coals as organometallic compounds, chelated species, or as adsorbed cations.

The number of generalisations that can be drawn decreases when organic affinities of coals from other parts of the United States are considered. However, Ge, B, and Br generally are among the elements with the highest organic affinities. Arsenic, in all cases, is among the elements with the lowest organic affinities. The variability in organic affinities between coals of eastern United States, western United States, and the Illinois Basin is sufficiently large that a prediction of the value of organic affinity of an element in a sample that is yet to be analysed is, very likely, imprecise.

The statistical analyses of the chemical analytical data that are given here and the observations made are a first step in the complete geochemical analyses of these data. Currently in progress are further statistical analyses, areal and stratigraphic mapping of the distribution of the elements, and correlation of the elemental distributions with mineral matter analyses and other geological features of the coal basin.

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APPENDIX

METHODS OF ANALYSIS

Introduction

The methods used in this project were instrumental neutron activation analysis (INAA), neutron activation analysis with radiochemical separation (NAA-RC), optical emission spectrochemical analysis--direct reading (OE-DR) and photographic (OE-P), atomic absorption analysis--flame (AA) and graphite furnace (AA-G), X-ray fluorescence analysis (XRF), and ion-selective electrode (ISE).

Methods developed and used in the initial project (EPA 68-02-0246) were detailed in the reports made on that project (Ruch et al., 1973, 1974). In general, the same multi-element method approach was continued with refinements and substitutions in most analytical disciplines.

In particular, for INAA a new higher resolution Ge(Li) detector, coupled with a 4096-channel analyzer system, replaced the NaI(Tl) detector and 400-channel analyzer. This greatly increased the scope and capability of NAA for the analysis of coal and coal-derived materials for trace elements, and fewer radiochemical separation procedures were required.

Both emission spectrochemical procedures were updated and refined through further optimization of exposure times, preparation of more suitable standards, and more extensive data processing.

Atomic absorption analysis was employed essentially as previously reported. One refinement was the use of new electrodeless discharge lamps (EDL's). Toward the latter part of this contract period, a more sensitive graphite furnace excitation technique was developed, and preliminarily evaluated for the determination of Cd, Tl, and Te.

The X-ray fluorescence, ion-selective electrode procedures, and conventional ASTM coal analysis methods used were essentially the same as those reported previously (Ruch et al., 1973, 1974).

Development of energy-dispersive X-ray fluorescence analysis of coal was begun during the project. The instrumentation consisted of an americium-241 excitation source; secondary targets of copper, molybdenum, tin and dysprosium; and a Si(Li) detector with a 1000-channel analyser.

It was estimated that the average relative standard deviation for any technique was in the range of 10 to 20 per cent for most elements concerned.

NEUTRON ACTIVATION ANALYSIS

Nondestructive neutron activation analysis, coupled with the high-resolution Ge(Li) detector, allowed the simultaneous determination of a large number (38) of trace elements in whole coal to the ppb level. The technique significantly increased the scope and capability of trace element analysis in coal and coal-derived materials. The technique eliminated the necessity for time-consuming radiochemical separations in the determinations of such elements as As, Sb, Br, Ga, and Se, as previously required when counting with the NaI(Tl) detector.

Comparison of INAA data obtained in this laboratory with the published data on NBS 1632, the Trace Elements in Coal standard (Table A), indicates generally good agreement and acceptable precision.

INAA Procedures

Approximately 1 gram of whole coal was weighed into two-fifths dram polyethylene vials, was heat sealed, and was activated in the TRIGA MKII reactor at the University of Illinois. The irradiation times, the decay interval, the count interval, the nuclide observed, and limits of detection for the elements determined are shown in Table B. Irradiation and counting times were chosen to optimise the determination of certain elements. All samples were compared to an irradiated multielemental standard, which was composed of a solution of reagent-grade materials evaporated onto Whatman 41 filter papers. In addition to the prepared standards, a sample of NBS-1632 standard reference coal was occasionally analysed in order to check the accuracy of the data in comparison to accepted literature values. The counting system is shown schematically in Figure A. Data reduction was accomplished with the IBM 360 facilities at the University of Illinois.

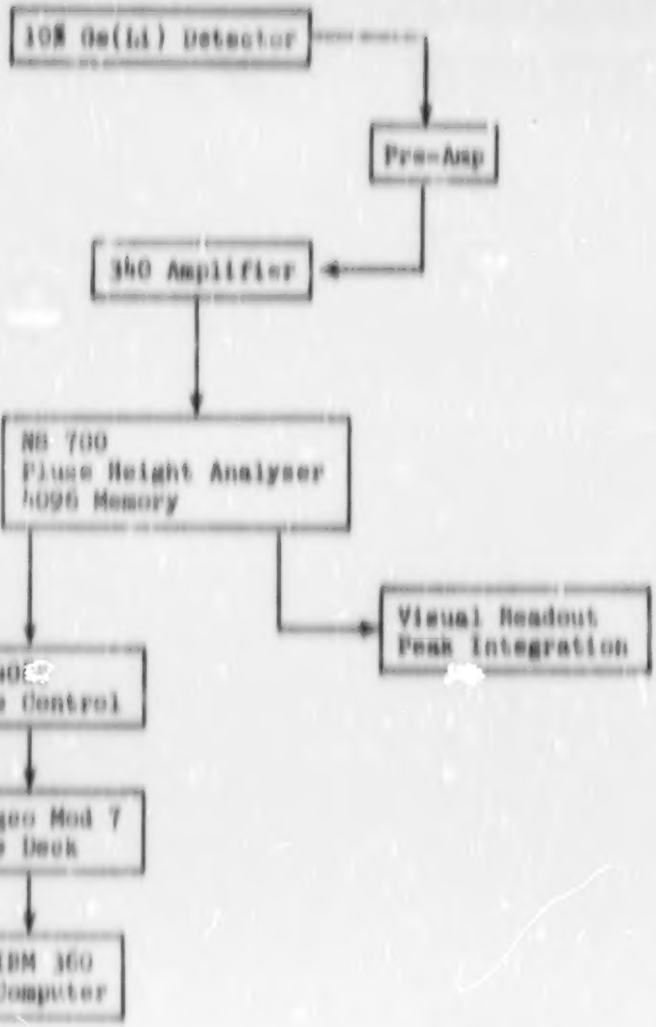
10% Ge(Li) Detector
Pre-Amp
340 Amplifier
NS 700
Pluse Height Analyser
4096 Memory
NS-40
Tape Control
Visual Readout
Peak Integration
Wangco Mod 7
Tape Deck
IBM 360
Computer

Fig. A - Schematic of instrumental neutron activation system.

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	3.8 ± 0.7	3.4 ± 0.2	2.1 ± 0.3	3.01 ± 0.28	3.8 ± 0.5		2.44 ± 0.39	2.8	3.2 ± 0.3
[illegible]				7.58 ± 0.14		40.			
[illegible]									
[illegible]	3.2 ± 0.4			0.22 ± 0.02				5.2	
[illegible]	<0.2	0.34 ± 0.03	[illegible]	1.05 ± 0.1					
[illegible]			1.74 ± 0.03	0.21 ± 0.02				<0.4	
[illegible]	0.76 ± 0.02	0.73 ± 0.10		0.23 ± 0.02	0.34 ± 0.07				
[illegible]				16.2 ± 1.0	125 ± 20			95.	
[illegible]									
[illegible]	3.4 ± 0.8	3.9 ± 1.3		3.09 ± 0.26	4.4 ± 1.8	2.2	3.15 ± 1.4	3.	
[illegible]									
[illegible]	10.8 ± 0.4	10.7 ± 1.2			11.3 ± 3.1	11.3	7.84 ± 0.75		
[illegible]	20.7 ± 2.7	19.5 ± 1			17.2 ± 3.3	20.	15.7 ± 0.39		
[illegible]					4.4 ± 1.5	10.7			
[illegible]	1.6 ± 0.2	1.7 ± 0.2			1.2 ± 0.18	4.7	1.38 ± 0.16		
[illegible]	0.38 ± 0.03	0.33 ± 0.04			0.37 ± 0.037	0.4	0.37 ± 0.02		
[illegible]						2.5	3.84 ± 0.28		
[illegible]		0.27 ± 0.05			1.73 ± 0	0.5	0.48 ± 0.02		
[illegible]	1.59 ± 0.18				0.85 ± 0.06	1.4	1.38 ± 0.09		
[illegible]	0.74 ± 0.09	0.7 ± 0.1			0.88 ± 0.04	0.8	0.88 ± 0.04		
[illegible]	0.73 ± 0.03	0.74 ± 0.1			0.476 ± 0.017	0.1	0.12 ± 0.005		
[illegible]	3.5 ± 0.6	3.2 ± 0.7	(3.0)		3.7 ± 0.2	3.2	1.28 ± 0.09		
[illegible]	1.10 ± 0.2	0.86 ± 0.05			1.82 ± 0.05	1.1	3.55 ± 0.32		
[illegible]	0.27 ± 0.02	0.29 ± 0.04			0.39 ± 0.029	0.3			
[illegible]	1.87 ± 0.20	0.75 ± 0.17			7.8 ± 0.6				
[illegible]	<0.007				2.748 ± 0.048				
[illegible]			1.72 ± 0.03	0.1	3.85 ± 0.35		3.23 ± 1.02	0.16	0.37 ± 0.17
[illegible]			30 ± 5	30.1 ± 1.6		25.			
[illegible]			2.58 ± 0.43	0.51 ± 0.26					
[illegible]			(40.1)	7.02					
[illegible]					2.40 ± 0.27				
[illegible]						0.3			
[illegible]								45.	
[illegible]								110.	

TABLE 8—DETECTION LIMITS AND NUCLEAR PROPERTIES OF ISOTOPES USED FOR THE ANALYSIS OF COAL

Element	Isotope Produced	Half Life	Cross Section (barns)	Counting Period*	Major gamma-rays utilized (keV)	Limit of Detection (ppm)	Average Relative Standard Deviation %
Na	^{24}Na	15 hr	0.53	A, B, C	1368	0.5	5
Cl	^{38}Cl	37 min	0.56	A	1642	25	15
K	^{42}K	12.5 hr	1.2	B, C	1525	30	15
Sc	^{46}Sc	83.9 day	11	D	889, 1120	0.01	5
Cr	^{51}Cr	27.8 day	17	D	320	1	10
Mn	^{56}Mn	2.58 hr	13.3	A, B	846, 1811	0.1	5
Fe	^{59}Fe	45 day	1.1	D	1099, 1292	200	10
Fe	^{54}Mn	291 day	0.8	D	835	1000	15
Co	^{60}Co	5.26 yr	37	D	1173, 1333	0.5	5
Ni	^{58}Co	71 day	0.2	D	810	5.0	20
Zn	^{65}Zn	245 day	0.5	D	1115	5.0	20
Zn	^{69}Zn	13.8 hr	0.1	B, C	439	50	25
Ga	^{72}Ga	14.2 hr	5.0	B, C	834, 630	0.5	15
As	^{76}As	26.5 hr	4.5	C	559, 657	0.2	20
Se	^{75}Se	120 day	30	D	136, 265	0.1	15
Br	^{82}Br	35.3 hr	3.0	B, C	554, 777	0.5	20
Rb	^{86}Rb	18.7 day	0.7	D	1078	1.0	20
Sr	^{87m}Sr	2.8 hr	1.3	A, B	388	5.0	10
Ru	^{97}Ru	67 hr	0.15	C	191	5.0	20
Ag	^{110m}Ag	253 day	1.5	D	657, 937	1.0	20
Cd	^{115}Cd	53 hr	0.3	C	528	5.0	50

TABLE 8—Continued

Element	Isotope Produced	Half Life	Cross Section (barns)	Counting Period*	Major gamma-rays utilized (keV)	Limit of Detection (ppm)	Average Relative Standard Deviation %
In	^{116m}In	54 min	155	B	417, 1097	0.01	20
Sb	^{122}Sb	2.7 day	6.5	C	564	0.2	20
Sb	^{124}Sb	60.2 day	2.5	D	1691	0.1	10
I	^{128}I	25 min	6.2	A	443	0.5	25
Cs	^{134}Cs	2.05 yr	31	D	797,569	0.05	15
Ba	^{131}Ba	12 day	8.8	C, D	496, 216	20	15
Ba	^{139}Ba	83 min	0.35	A, B	166	200	20
La	^{140}La	40.2 hr	8.9	C	1596, 487, 329	0.1	5
Ce	^{141}Ce	33 day	0.6	D	145	0.5	15
Sm	^{153}Sm	47 hr	210	C	103	0.05	5
Eu	^{152m}Eu	9.3 hr	2800	A, B, C	122, 344, 963	0.10	5
Eu	^{152}Eu	12.5 yr	5900	D	1408	0.05	5
Tb	^{160}Tb	72 day	46	D	879, 1178	0.05	10
Dy	^{165}Dy	2.35 hr	700	A,B	95, 361, 633	0.1	10
Yb	^{175}Yb	4.2 day	55	C	396, 282	0.5	25
Yb	^{169}Yb	32 day	5500	D	198, 110	0.1	10
Lu	^{177}Lu	6.7 day	2100	C	208	0.05	15
Hf	^{181}Hf	42.5 day	10	D	481, 133	0.05	15
Ta	^{182}Ta	115 day	21	D	155, 222, 1221	0.01	10
W	^{187}W	23.8 hr	40	B, C	480, 686	0.2	20

TABLE 8—Concluded

Element	Isotope Produced	Half Life	Cross Section (barns)	Counting Period*	Major gamma-rays utilized (keV)	Limit of Detection (ppm)	Average Relative Standard Deviation %
Au	^{198}Au	65 hr	99	C	411	0.01	50
Th	^{233}Pa	27 day	7.5	D	312	0.2	10
U	^{239}Np	56 hr	2.7	C	277, 228	0.1	20

* Counting Period	Irradiation	Flux (n.cm⁻².sec⁻¹)	Decay Interval	Count Interval
A	15 min	2.0×10^{12}	10 min	100 sec
B	15 min	1.0×10^{12}	2 hr	2000-3100 sec
C	2 hr	1.1×10^{12}	25 hr	4000-7000 sec
D	2 hr	5.1×10^{12}	15 day	5-10 hr

Radiochemical Separation Procedure for Mercury

Instrumental neutron activation analysis was not satisfactory for the determination of Hg at the levels usually found in whole coals (0.01 to 0.50 ppm). Hence, use of the radiochemical procedure described by Ruch et al., (1974), a method previously modified from that of Rook, Gills and LaFleur (1971), was continued. This procedure differed from that of Rook, Gills, and LaFleur (1971), in that the combustion products, including Hg, were collected in a cold-trap cooled by dry ice instead of liquid nitrogen.

Neutron Activation Analysis of Tellurium

Tellurium cannot be determined in coal by instrumental neutron activation analysis because tellurium has poor nuclear characteristics for analysis and normally occurs only in such small amounts (0.02 to 0.1 ppm) that interferences from other isotopes present prevent its detection.

A radiochemical separation procedure was proposed involving the decay of ^{131}Te to ^{131}I after irradiation of the coal-ash. ^{131}I was collected by solvent extraction and its activity was measured. From standards, the limit of detection of Te was estimated at 0.1 to 0.4 ppm. The results were corrected for the ^{131}I produced by fission of ^{235}U--sometimes a serious interference. Because the expected levels of Te in coal appeared to be about the same as the detection limits, the procedure did not hold sufficient promise to be pursued. It would be possible to lower the limit of detection by increasing the time of irradiation from the normal two hours to 10 to 20 hours. This was not practical. At present, other methods such as AA (graphite furnace) and nondispersive XRF are being investigated.

Neutron Activation Analysis of Thallium

A radiochemical separation procedure was developed to determine Tl in coal-ash. The method involves sodium hydroxide fusion, sulfide precipitation, solvent extraction, and final precipitation of TlI with counting for ^{204}Tl done on the precipitate. The technique was rather lengthy since ^{204}Tl emits only beta activity. The measurement is susceptible to interference from even very low amounts of other radioactivity. The limit of detection with a 20-hour irradiation was only 2 ppm Tl in whole coal, thus the procedure is inadequate and impractical for the expected range of 0.1 to 1 ppm Tl in coal.

EMISSION SPECTROCHEMICAL ANALYSIS

Preparation of high-temperature (500°C) coal-ash was described in detail in Ruch et al., (1974), p. 60-65. Two grams of coal were weighed into a used silica crucible and were dried. The dried coal was ashed in the covered crucible at 500°C for approximately 20 hours, with occasional mixing with a platinum wire. The cooled, weighed ash was ground until homogeneous in a mullite mortar and pestle, then dried at 110°C for a few hours.

A set of synthetic standards was prepared by using the average concentrations of Si, Al, Ca, Fe, K, Mg and Na, and by using average per cent for high-temperature ash; the average values were taken from 82 previously analyzed Illinois coals. The concentration values were calculated to their oxide or carbonate equivalents on the ash basis, the type of calculation depending upon the expected combination of each element in high-temperature coal ash. These concentrations were then normalized to 100 per cent. The selected compounds and their concentrations are listed in Table C.

Ten grams of the mixture were prepared and were mixed in a mixer-mill for one hour in an alumina ceramic container.

Portions of this coal-ash base were then mixed with amounts of SiO_2- and Al_2O_3-based Spex Time-Saver Standards, which contain 1000, 333, 100, 33, and 10 ppm of the 49 trace elements of Spex Mix 1000 (Spex Industries, Inc., Box 798, Metuchen, NJ 08840) such that the SiO_2:Al_2O_3 concentration ratio was equal to 2.22. The amount of each Spex Mix standard used is shown in Table D.

TABLE C—SYNTHETIC COAL ASH BASE

Compound	Percent of Total Coal Ash Base (W/W)
SiO_2	38.30
Al_2O_3	18.15
$CaCO_3$	15.55
Fe_2O_3	21.19
K_2CO_3	2.20
MgO	0.61
Na_2CO_3	0.99
Total	99.996

TABLE D—COAL ASH STANDARDS

Designation	Coal Ash Standard Final Concentration (ug/gm)	Weight of Coal Ash Base (mg)	Spex Standard Concentration (ug/gm)	Weight SiO_2 Spex Standard (mg)	Weight Al_2O_3 Spex Standard (mg)
CA-1	333	667.0	1000	229.0	103.0
CA-2	100	900.0	1000	69.0	31.0
CA-3	33.3	900.0	333	69.0	31.0
CA-4	10	900.0	100	69.0	31.0
CA-5	10	900.0	33	69.0	31.0
CA-6	1.0	900.0	10	69.0	31.0

The mixture used for loading the spectrometer electrodes consisted of 40 mg of sample or standard, 10 mg of spectroscopically pure $Ba(NO_3)_2$, and 150 mg of SP-2X graphite powder. These were mixed together on a Wig-L-Bug shaker for 60 seconds in a 2.54 cm in length by 1.27 cm in diameter plastic vial containing two plastic balls .32 cm in diameter. This mixture was then weighed in the appropriate amounts for loading into electrodes. The spectroscopic parameters used are listed in Table 6.

TABLE 6—SPECTROSCOPIC PARAMETERS

Instrument	Jarrell-Ash 1.5 m Ebert spectrograph	Jarrell-Ash .75 m direct reading spectrometer	Jarrell-Ash .75 m direct reading spectrometer
Arc current (D.C.)	10A	15A	7.5A
Arc Gap	4mm	4mm	4mm
Exposure time	60 sec.	65 sec.	30-80 sec.
Atmosphere and flow rate	80% argon, 20% oxygen at 15 SCFH	80% argon, 20% oxygen at 10 SCFH	80% argon, 20% oxygen at 15 SCFH
Sample electrode	National L-3903 under-cut	National L-3979 thin-wall crater	National L-4006 necked crater 3/16 inch diameter
Counter electrode	National SP-1009	National L-4036 (ASTM C-1)	National L-4036 (ASTM C-1)
Electrode charge	20 mg	15 mg	10 mg
Entrance slit width	10 um	10 um	10 um
Photographic plate and developer	SA-1 D-19		
Step sector	6 step, 2:1 ratio		
Internal standard		Pd, variable internal standard	
Exit slit width		50 um	50 um

Direct-Reading Spectrometer Procedures

Time-intensity curves were run by the use of standards to determine the proper exposure time for the desired spectral lines. After the exposure time was determined, more standards were arced to establish a calibration curve for each element desired and to apply the proper electronic corrections to each element readout module. The data received from the instrument were relative intensities, standardized by using a spectral line resulting from variable, but known, concentrations of iron. Usually, four electrodes were arced for each sample.

The coordinates of each point used in an element calibration curve were treated by least squares regressions to determine the coefficients of the first or second degree equation that best described the particular calibration curve. By the use of the relative intensity data for unknown samples and the calibration curve coefficients, the concentration of each desired element in the electrode sample was calculated by the use of a computer program. These results were calculated to the whole coal basis. The means, standard deviations, and relative standard deviations calculated, and the final results were printed out. The computer program has saved approximately 30 percent of the time that was formerly taken to complete the analysis and data treatment of coal-ash samples.

3.4 Meter Ebert Spectrograph Procedure

When using the photographic instrument, time-intensity studies were again performed to attain the optimum exposure time for the determination of 14 elements in the same sample mixture by the use of one analysis program.

The same sample and standard mixtures were used for photographic and for direct-reading spectroscopy. The percent transmittance values of the analytical lines were determined by standard densitometry.

A computer program was written to speed the data handling for this procedure. One portion of the program was used to determine the relative intensity of a spectral line from its percentage of transmittance and the corresponding spectral step. A Hurter-Driffield (H-D) emulsion calibration plot was used for this procedure by plotting the percentage of transmittance versus exposure step number. An inverted logarithmic abscissa was overlain on the step number abscissa and a relative intensity of 1.00 at 50 percent transmittance was arbitrarily assigned. Because the H-D plot was sigmoid, and to our knowledge there was no single equation that describes this type of curve well, a spline function routine was used for mathematical fitting. Data points for the H-D plot were spaced every 2 percent of transmittance. The curve fitting routine determined which interval to use for the unknown percent of transmittance value, fitted a quadratic equation to the interval from the calibration data, and calculated the resulting relative intensity of the unknown spectral line. The relative intensity was then handled in a manner similar to that used for the direct-reader data. That is, the relative intensity of a given unknown spectral line was operated upon by the coefficients of the respective element calibration curve to determine the concentration in the electrode mixture and then to determine the concentration in the whole coal. Two electrodes per sample were arced in the photographic method. The computer programming step saved about 50 percent of the time for analysis of a sample for 14 elements.

Table F lists the elements determined, the method used, the detection limit, the concentration range, and the average relative standard deviations for elements in whole coals in this study.

Special Refinement of Optical Emission Procedures

1. A new method for the determination of thallium was sought by both direct-reading and photographic optical emission spectroscopy. A photomultiplier was installed in the direct reader and aligned for the Tl I 3775.72 A line. Standards were arced to determine a calibration curve using the same procedures as described previously. The detection limit found for these parameters was 33ug/gm in ash. Thallium was sought in several coal-ash samples but was not detected.

Standards were arced for photographic detection, and a calibration curve was drawn for the Tl I 2768 line. The sample mixture and arcing conditions were the same as described previously. The detection limit was 33ug/gm in the ash, but the sensitivity was good. Again, thallium was sought in several coal samples but was not detected.

An optical emission (direct-reading) spectrometry procedure for thallium determination in coal-ash was investigated and found applicable. The high-temperature ash (HTA) of a coal was mixed 1:1 by weight with a 20 percent sodium chloride - 80 percent graphite mixture (sodium chloride catalog 1352 and SP-2-X grade graphite, Spex Industries, Inc., Box 798, Metuchen, NJ 08840) in polystyrene vials, 1/2 inch in diameter by 1 inch deep, containing 2 methacrylate balls, 1/8 inch in diameter. Then the vials were placed in a Wig-L-Bug and agitated for one minute.

Next, 10 mg of the charge mixture was weighed and was loaded into each of three necked crater electrodes (3/16 inch in diameter, National type L-4006, Spex Industries, Inc.). The counter electrode (1/8 inch in diameter, National type L-4036, Spex Industries, Inc.) and sample electrode were then placed in the arc stand of a Jarrell-Ash Model 750 Atomcounter.

TABLE F—EXPERIMENTAL PARAMETERS AND RESULTS FOR OE-P AND OE-DR

Element	Wavelength (Å)	Method	Concentration Range Whole Coal (μg/gm)	Average Relative Standard Deviation (%)	Detection Limit in Ash (μg/gm)
Ag	3280.7	OE-P	0.01 - 2.5		
B	2496.8 (2nd order)	OE-D	5 - 268	8.8	1
Be	2348.6 3131.07	OE-D OE-P	0.1 - 5.5 0.15 - 3.5	7.8	0.2
Cd	2288.0	OE-D	<0.1 - 20	16.7	0.7
Co	3453.5 3453.5	OE-D OE-P	0.5 - 18 0.5 - 16	5.65	0.3
Cr	4254.3 2843.25	OE-D OE-P	2 - 62 1.6 - 58	7.9	0.5
Cu	3274.0 3274.0	OE-D OE-P	2 - 59 5.0 - 111	8.9	0.5
Ge	2651.2 3039.1	OE-D OE-P	<0.1 - 12 <0.35 - 16	16.5	0.6
Mn	2605.7	OE-P	1.6 - 180		
Mo	3170.3 3170.3	OE-D OE-P	<0.1 - 29 <0.11 - 32	10.1	0.3
Ni	3414.8 3414.8	OE-D OE-P	2 - 52 1.3 - 58	8.7	0.6
Pb	4057.8 2833.1	OE-D OE-P	<1 - 180 1.0 - 65	16.3	10
Sr	4607.3	OE-D	11 - 270	11.0	1
Tl	2767.9	OE-D	.1 - 1.3	16.0	0.3
V	3183.9 3185.4	OE-D OE-P	5 - 90 5.8 - 158	7.0	3.3
Zn	2138.5 3345.0	OE-D OE-P	<1 - 191 <0.6 - 690	12.3	1
Zr	3392.0 3392.0	OE-D OE-P	9 - 67 16 - 109	8.1	3.3

The sample was arced until it was visually apparent that the alkali metal vapor phase of the arc had significantly decreased. While the sample was arcing the "instantaneous" response signal from the TI 3775 photomultiplier tube was recorded on a strip chart recorder. The resulting strip chart peak (approximately 3 to 8 seconds after arc ignition) was measured and was compared to a calibration curve derived from synthetic coal-ash standards (Tables C and D) where peak height vs. concentration in microgram per gram was plotted on log-log paper.

2. A carrier distillation method for molybdenum was attempted by the use of photographic detection. The coal-ash standards were mixed into a matrix of SiO_2 containing 10 percent Ga_2O_3 as a carrier. This method was found to be unsatisfactory.

3. Photographic plates were sprayed with a solution of sodium salicylate in absolute ethanol and were allowed to dry. It was hoped that the sodium salicylate would increase the sensitivity of the SA-1 plates to the ultraviolet region by fluorescing under UV radiation. Sodium salicylate fluoresces in the blue region, a very satisfactory wavelength region for the SA-1 emulsion. However, when standards containing 333 ppm to 3.3 ppm cadmium were arced, no spectral line could be detected at CD I 2288A, even for the high concentration standards.

ATOMIC ABSORPTION ANALYSIS

Flame Atomic Absorption Analytical Procedures

Atomic absorption (AA) methods were used for the determination of Cd, Cu, Ni, Pb, and Zn in low-temperature ashed fractions of whole coal, bench, and float-sink samples. The analytical procedures used in this study were those reported by Ruch et al., (1974) with a few modifications. The methods are summarized below.

Atomic absorption measurements were made using a Perkin- Elmer Model 306 Atomic Absorption Spectrophotometer. Absorbance signals were recorded on a strip chart recorder. An air-acetylene flame was used with a 4 inch in length single-slot flat-head burner. Standard single element hollow cathode lamps were used for all elements but occasionally Cd and Pb electrodeless discharge lamps were used. Corrections for non-atomic background absorption were made simultaneously by use of a deuterium arc background corrector.

All reagents used were ACS certified reagent grade chemicals, and standard stock solutions were prepared from high purity metals or compounds. The calibration standards were prepared from diluted stock solutions that contain the following matrix materials: 1% V/V 48% HF, 1.4% V/V aqua regia (1:3:1; HNO_3-HCL-H_2O), and 1% W/V H_3BO_3.

Approximately 0.1 g of low-temperature ashed sample, previously dried at 110°C for several hours, was transferred to a 50 ml or 125 ml linear polyethylene screw-cap bottle. The sample was wetted with 1 ml of 1:1 distilled HCl and was dried in a steam bath. The dried sample was then wetted with 0.7 ml aqua regia and 0.5 ml of HF was added. The bottle was capped tightly and was placed on a steam bath for approximately two hours. After the bottle was removed from the steam bath and was allowed to cool, 10 ml of a 50 g/l H_3BO_3 solution was added. The dissolved sample was transferred to a 50 ml Pyrex volumetric flask, was diluted to volume with deionized water, and was returned to the bottle for storage.

The flame absorption analytical conditions are presented in Table 6. In the case of Zn, where solution concentrations were sometimes large enough to cause a departure from linearity in a plot of absorbance versus concentration, the burner was rotated from its usual parallel orientation in order to decrease the sensitivity, and thereby overcome the necessity for sample dilution. Final concentrations were calculated by solving for concentration in a least squares constructed calibration curve of absorbance versus concentration. A new calibration curve was calculated for each set of analyses.

The relative standard deviation was estimated to average 10 percent or less for the determinations discussed.

TABLE 6—FLAME ATOMIC ABSORPTION PARAMETERS

Lamp	Current or Power	Wave-length (nm)	Slit (nm)	Burner Position	Typical Sensitivity (ppm/0.0044 Abs)	Solution Concentration Range (ppm)	Detection Limits in Ash (ppm)
Cd HCL	8ma	228.8	0.7	parallel	0.021	0.005 to 1.8	1.5
Cd EDL	5w	228.8	0.7	parallel	0.015	0.002 to 1.2	1
Cu HCL	10ma	324.7	0.7	parallel	0.07	0.005 to 5	2.5
Ni HCL	10ma	232.0	0.2	parallel	0.1	0.007 to 3.5	1.5
Pb HCL	10ma	283.3	0.7	parallel	0.5	0.01 to 20	15
Pb EDL	11w	217.0	0.7	parallel	0.18	0.02 to 4.5	10
Zn HCL	15ma	213.9	0.7	parallel	0.18	0.005 to 0.6	2
Zn HCL	15ma	213.9	0.7	up to 90° from parallel	0.2	0.6 to 10	

Graphite Furnace Procedures

Because low-temperature ash samples often have concentrations of cadmium, which were undetectable by flame atomic absorption, and because of the need for analytical methods for the determination of tellurium and thallium, the use of flameless atomic absorption spectrometry was investigated. The major advantage offered by flameless atomisation schemes such as the graphite tube atomiser was that the sensitivities and detection limits are often 100 to 1000 times better than with flame atomisation for most metals. This was due, to a large extent, to the greatly increased residence time of the atomic vapor in the optical path and also to the total sample being available for absorption. The major disadvantages in this method were that it was more subject to severe interferences and that it was much more time consuming than flame methods.

The flameless atomiser used in this investigation was a Perkin-Elmer HGA-2000 Graphite Furnace used in conjunction with a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer. Absorbance signals were recorded on a strip chart recorder. Corrections for broad band absorption were made with a deuterium arc background corrector. Electrodeless discharge lamps were used for tellurium and thallium determinations, and a hollow cathode lamp was used for cadmium.

Low temperature ash samples were prepared in exactly the same manner as the flame atomic absorption procedures. These methods appeared to be quite adequate for the determination of cadmium and tellurium, but severe matrix interferences were found to be present for thallium, as will be discussed later. To compensate for any matrix interferences that might occur in the determinations, the method of standard additions was used for all three elements. The standard additions were made directly into the furnace following the addition of the sample solution. The analytical conditions developed for this study are summarised in Table H.

The determination of cadmium by the use of the graphite furnace is relatively straightforward with only minor matrix interferences. Good absorbance signals were obtained over a range of atomisation temperatures from 1800°C to 2300°C with maximum absorbance between 2000°C and 2100°C. Broad band absorption was relatively small (0.075 absorbance units) even at charring temperatures as low as 150°C, and the maximum charring temperature, without Cd atomisation, was 900°C. An examination of Table I shows that the accuracy for Cd determination by this method was high, and the agreement with other published values for NBS Standard Reference Material 1632 was good. The relative standard deviation was approximately 5 percent.

The determination of tellurium with the graphite furnace was also relatively straightforward, although there were some interferences.

TABLE H—HGA-2000 ANALYTICAL CONDITIONS

Element	Cd	Te	Tl
Source	HCL	EDL	EDL
Current or Power	8mA	7.0w	5.0w
Wavelength (nm)	228.8	214.3	276.8
Slit (nm)	0.7	0.2	0.7
Purge gas/flow (l/min)	Ar/1.0	Ar/1.0(interrupt)	Ar/1.0
Drying time (sec)	30	30	30
Drying temperature (°C)	100	100	100
Charring time (sec)	20	20	20
Charring temperature (°C)	300	500	300
Atomization time (sec)	8	8	8
Atomization temperature (°C)	2000	2500	2300
Background correction	D_2	D_2	D_2
Typical sensitivity (pg/.0044 Abs)	2.5	21	200
Typical detection limit (ppm) (ash, 20 ul sample)	0.05	1.0	5.0

TABLE I—COMPARISON OF RESULTS FOR Cd, Te, AND Tl IN NBS SRM 1632

SOURCE	Cd	Te	Tl
NBS	0.19±0.03	(<0.1)	0.59±0.03
Klein, et al. (1975)	0.21	- - -	- - -
Chattopadhyay (1978)	0.20±0.02	1.02	0.51±0.06
This study	0.21±0.01	0.5	<2.0

( ) informational value

The best absorbance signals were obtained at atomisation temperatures above 2400°C. Broad-band absorption was also relatively small, even at temperatures as low as 150°C, and the maximum charring temperature before any loss of Te was approximately 900°C. It was observed that the sample matrix, including the reagents used, in the dissolution, impart an enhancement of nearly 40 per cent in the peak-height absorbance and is accompanied by a narrowing of the absorbance peak relative to the same concentration of Te in a one per cent HNO_3 matrix. It was not determined whether the areas under the two peaks were equivalent.

Tellurium was approximately one tenth as sensitive as Cd. In the samples analysed in this study, it was often difficult to reliably differentiate the absorbance peak from the baseline. At these low Te levels, the precision was poor.

Thallium was subject to very severe matrix interferences that, if left unimproved, rendered thallium nearly undetectable in the sample. In an examination of the contributions of reagents to these interferences, it was found that the HCl in the aqua regia was one of the major contributors. Tl in a one percent HCl matrix has an absorbance of only two per cent of that found in a one percent HNO_3 matrix. The absorbance was improved to only 30 per cent for a 0.0001 per cent HCl matrix. Such interference by HCl for Tl has been observed by Welcher et al. (1974), and Fuller (1976) The present study showed that matrices containing one per cent H_3BO_3 and one per cent HF reduce Tl absorbance by nearly 50 per cent.

In attempting to overcome HCl interference, Fuller (1976) suggested the addition of one per cent (v/v) H_2SO_4 as a means of improving sensitivity and observed that H_2SO_4 was more effective than HNO_3 for samples with very simple matrices. For the low-temperature ash matrix used in this study, the reverse was observed; concentrated HNO_3 was found to be the most effective in removing the interference. It was also observed in this study that the simple addition of HNO_3 to the sample was not as effective as drying the sample first in the graphite tube, and then adding the HNO_3. Such a procedure resulted in a thallium absorbance for the sample-reagent matrix that was about 50 per cent of that observed in the HNO_3 matrix alone.

The cause of this chloride interference has been suggested by Fuller to be due to the possible formation of a volatile chloride when using HCl, leading to a loss of thallium before atomisation. It was observed in the present study that if thallium was volatilised, then no greater than 50 percent of it was lost during a drying stage at 150°C for 30 sec, as is shown by the effectiveness of the HNO_3 addition after the samples were dried. Continuous monitoring of thallium atomisation losses during drying and charring stages has thus far shown no loss. It would appear that the chloride interference mechanism was more complex than that suggested by Fuller. These interferences were not investigated thoroughly, but further work is continuing.

X-RAY FLUORESCENCE ANALYSIS OF WHOLE COAL

X-ray fluorescence determinations were made on whole coal for As, Br, Pb, Zn, Cu, Ni, P, Cl, S, V, Mg, Ca, Fe, Ti, Al, and Si. A Philips vacuum spectrometer equipped with a Mark I solid-state electronics panel was used for all analyses.

A 3Kw chromium X-ray tube was used and the procedures were as described by Ruch et al. (1973, 1974). Further discussion of the methods was presented by Kuhn et al. (1975). The only change in the procedure has been the use of a new diffracting crystal with better sensitivity for the elements determined. A TlAP crystal replaced the EDDT crystal for the determination of elements in the periodic table from Na through Si.

Whole coal was used for the preparation of samples for analysis and all results are given on the dry whole coal basis.

As detailed in the previous report, the observed relative standard deviations for elements determined by this technique ranged from 0.35 to 8.4 percent.

SUMMARY OF METHODS

Tables J and K summarize those analytical methods the results of which were finally incorporated into the final values for elemental composition of whole coal, bench samples, and float-sink samples. In general, the same techniques were applied to whole coal and bench samples. However, the varying matrix of the float-sink samples required different analytical procedures in some cases.

When an element was determined by two or more methods, all the results were not necessarily used to calculate the "most probable" concentration. It was suspected that results for some elements by a particular method might be biased because of interferences. For example, it was known that in XRF, matrix effects inhibit the accurate determination of some trace elements, and in INAA the determination of some elements is susceptible to interference caused by the fact that the measured isotope is also produced by a nuclear reaction involving a second element.

ELEMENTS DETERMINED BY TWO OR MORE ANALYTICAL METHODS

The following comments summarize observations and decisions where an element was determined by two or more methods.

TABLE [illegible].—ANALYTICAL PROCEDURES USED TO DETERMINE TRACE ELEMENT VALUES IN WHOLE COAL AND [illegible] SAMPLES

Element	Procedure
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

TABLE [illegible].—ANALYTICAL PROCEDURES USED TO DETERMINE TRACE ELEMENT VALUES IN FLOAT-SINK SAMPLES

Element	Procedure
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]
[illegible]	[illegible]

Beryllium- OE-P and OE-DR data were in good agreement and were averaged.

Bromine - Average of INAA and XRF data. Agreement between the methods was good for moderate to high values. For the low values INAA data were preferentially used because the technique had better sensitivity.

Cadmium - Average of AA and OE-DR data. Where there was a choice of lower limits or a choice between lower limits and a real value, the AA value was usually chosen. In general, the agreement was good between the two techniques. The recently developed OE-DR procedure proved to be very effective.

Chlorine - Average of INAA, XRF, and ASTM data. In general, the XRF values were slightly higher and the INAA values were slightly lower than the ASTM data. Only XRF data were used for float-sink samples.

Chromium - Average of INAA, OE-DR, and OE-P data. Agreement among the three methods was good. In a few instances, INAA appeared to have a high bias.

Cobalt - INAA, OE-P, and OE-DR data were in excellent agreement. Results by these methods were averaged.

Copper - Average of AA, OE-P, and OE-DR data. In general, the agreement was good. The XRF data were excluded because of a consistently high bias.

Germanium - Average of OE-P and OE-DR data. In those cases where an uncertainty arose, the OE-DR results were usually chosen.

Iron - Average of INAA and XRF data. The agreement was only fair between the two methods. The INAA data tended to have a high bias in a number of samples. Only the XRF data were used for the float-sink samples.

Lead - Average of OE-P and AA data. In those cases where a choice of limits existed, the AA results were usually chosen. In general, the two sets of data were in good agreement. Since LTA (150°C) was used for AA, and since HTA (500°C) was used for OE-P, this confirms previous findings that Pb appears to be quantitatively retained in the high-temperature ash sample.

Manganese - Average of INAA and OE-P data with good agreement. Samples C-18820 through C-19000 are based on OE-P results only.

Molybdenum - Average of INAA, OE-P, and OE-DR data. The INAA data occasionally tended to have a high bias at the lower values. The agreement among the three techniques was only fair. The XRF data were not used since they were neither consistent nor comparable.

Nickel - Average of AA, OE-P, OE-DR, and XRF data. The agreement was generally good among the four techniques with XRF results occasionally being excluded for having a high bias.

Potassium - Average of INAA and XRF data. Agreement was good for the two techniques. Only the INAA data were used for clay- and rock-type samples in the bench sets.

Sodium - Average of INAA and XRF data. Agreement was very good at moderate to high concentrations. At the lower concentrations INAA data were chosen because of greater sensitivity. Only the INAA data were used for float-sink samples.

Strontium - Average of OE-DR and INAA data. The methods agreed well in the low to intermediate concentrations; at higher concentrations, the INAA results were usually used.

Vanadium - Average of XRF, OE-DR, and OE-P data with only fair agreement. Some INAA results were obtained on several samples for confirmation.

Zinc - Average of AA, OE-P, OE-DR, and XRF data. The agreement among the four techniques was only fair owing to inhomogeneity of the samples for Zn. INAA results were not considered because of resolution problems.

Zirconium - Average of OE-P and OE-DR data with good agreement.

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